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REVIEWS

IX. *Atmospheric Absorption of Heat Radiation by Water Vapour.*

By T. G. COWLING*.

[Received September 23, 1949.]

SUMMARY.

The absorption of heat radiation by water vapour in the atmosphere is considered. It is shown that existing experimental results are all consistent with Lorentz collision-broadening. A law is derived for the variation of absorption with amount of water vapour; this law differs somewhat from that proposed by Elsasser, indicating a slower extinction of radiation than the latter. The correction for pressure variations is found to be greater than Elsasser's normally; the temperature correction agrees with his.

§ 1. IN an earlier report, the author has discussed the absorption of long-wave (heat) radiation by water-vapour in the atmosphere. The quantity of prime interest in that report was the fractional absorption A in relatively narrow wavelength ranges which are, none the less, sufficiently wide each to contain several absorption lines. The variation of A with the quantity w of absorbing vapour, with the pressure p , and with the temperature T , was given special attention. In the present paper, further experimental results regarding this variation are collected together, and are compared with the results of theoretical investigations.

The variation of A with w is found to follow a law somewhat different from that given by Elsasser (1942). It cannot be expressed by any simple analytical formula, and is best exhibited graphically. Plotting A directly against w is, however, inconvenient, since dA/dw rapidly falls off as w increases; it is preferable to plot A against $\log_{10} w$. The latter method of plotting, in addition to giving a more compact diagram, also has the advantage that an increase in the absorption coefficient in a definite ratio throughout the range leaves the form of the resulting curve unaltered, and simply displaces it bodily to left or right. This facilitates a comparison between the absorptions in wavelength ranges where the mean transparencies are very different, but where the types of absorption, as measured by the relative variations in the absorption coefficient throughout the ranges, may be expected to be similar.

The random effects of the distribution of strong absorption lines on the absorption curve are found to be smoothed out only if a frequency-range not much smaller than 25 cm.^{-1} broad is used. At frequencies where the mean transparency does not vary greatly, the range can, however, be 100 cm.^{-1} or more broad without any serious change in the absorption curve.

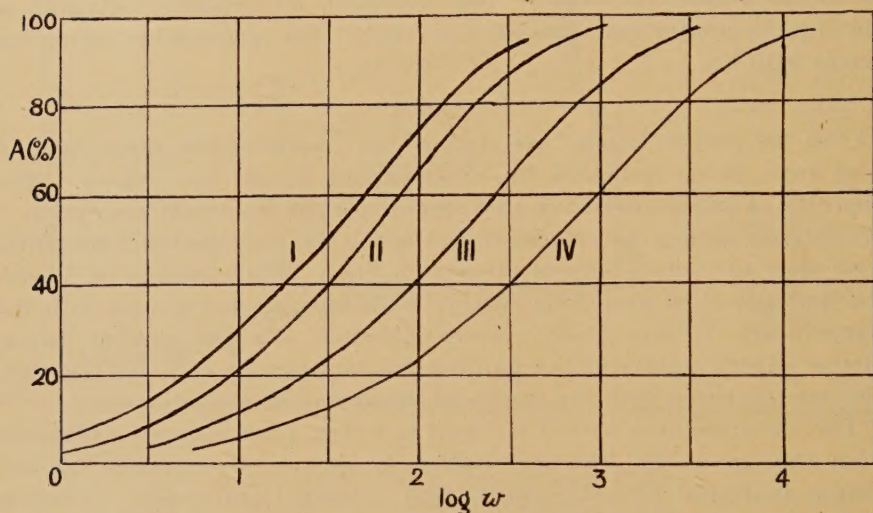
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§ 2. The following experimental studies have been made of the variation of A with w .

(i) The short-wave bands $\rho(0.94\mu)$, $\Phi(1.13\mu)$ and $\Psi(1.38\mu)$ have been studied by various authors in order to determine spectroscopically the total amount of water vapour present in the atmosphere. In fig. 1, curve I., are shown Fowle's (1912) results for Ψ' , giving the absorption in a range 0.021μ broad at 1.47μ . His results for ranges of similar breadths in the bands ρ and Φ give curves very like that for Ψ' .

The results obtained by other authors for these bands will not be considered in detail. Herzing's (1937) results referred to wavelength

Fig. 1.



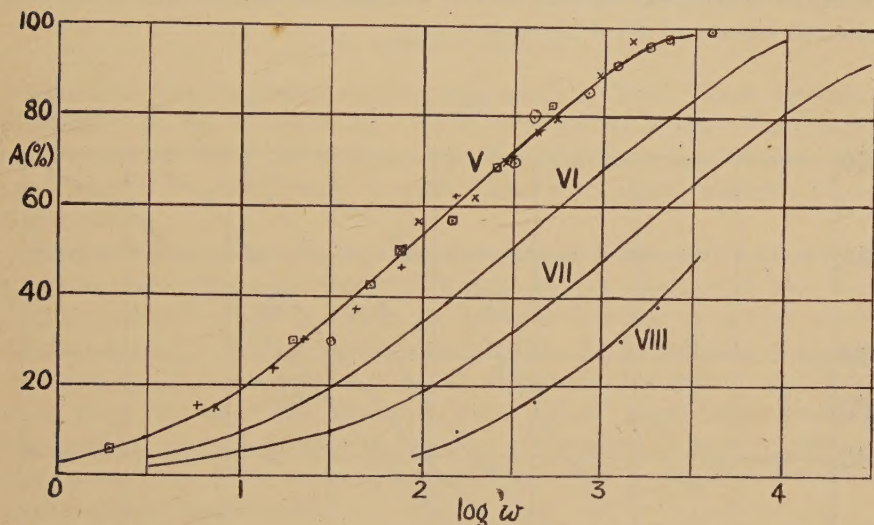
Graphs of absorption A against $\log w$. Curve I., Fowle's observed results for Ψ' ; curves II., III. and IV., calculated for the range $100-125 \text{ cm.}^{-1}$, with line-widths 0.4 , 0.2 and 0.1 cm.^{-1} . The unit of w is, for curve I., 0.316 cm. precipitable water; for curve II., $1.04 \times 10^{-5} \text{ cm.}$; for curve III., $5.2 \times 10^{-6} \text{ cm.}$; and for curve IV., $2.6 \times 10^{-6} \text{ cm.}$

ranges not small compared with the band width; Foster and Foskett (1945), on the other hand, appear to have used a very narrow range in studying the ρ -band (they do not state definitely its width, but speak of a range only a few Angstroms broad). Hand (1940) compared the absorption at the centre of the ρ -band with that at a neighbouring wavelength where the absorption, though much smaller, was not negligible.

(ii) The 6.3μ band has been studied by Fowle and Adel. Fowle (1917) made two bolograms (corresponding to $w=0.008$ and 0.082 cm. of precipitable water) with a 60° rock-salt prism; his remaining bolograms were made with much smaller resolution, using a 15° prism. In the latter bolograms, all the bands at wavelengths below 5μ were completely smeared out; even beyond 5μ there was a considerable mixing of wavelengths

which (because of the greater intensity of radiation in the shorter wavelengths) resulted in an apparent transfer of the absorption properties to higher wavelengths. We therefore use only the results of the 60° prism. These are combined with Adel's (1941) results for the transmission of sunlight through the atmosphere between 5.5μ and 14μ . Since absorption is almost complete between 5.7μ and 7μ , Adel's results give useful information only beyond 7μ . Near 7.75μ , Adel's curves show the absorption of water vapour overlaid by that of N_2O , but it is possible to obtain a reasonable estimate of that part of the absorption which is due to water vapour.

Fig. 2.



Graphs of absorption A against $\log w$. Curves V., VI. and VII., calculated for the range 225 – 250 cm.^{-1} , with line-widths 0.4 , 0.2 and 0.1 cm.^{-1} ; curve VIII., derived from Strong's experimental results at 21μ (the actual experimental results are shown by dots). The unit of w is, for curve V., $1.04 \times 10^{-5}\text{ cm.}$; for curve VI., $5.2 \times 10^{-6}\text{ cm.}$; for curve VII., $2.6 \times 10^{-6}\text{ cm.}$; and for curve VIII., 10^{-5} cm. Clustering round curve V. are shown Fowle and Adel's results for 7.25μ ($\odot$), 7.5μ ($\times$), 7.75μ ($\square$) and 8μ ($+$); the unit of w for these is, for 7.25μ , $10^{-2.6}\text{ cm.}$; for 7.5μ , $10^{-1.975}\text{ cm.}$; for 7.75μ , $10^{-1.4}\text{ cm.}$; and for 8μ , $10^{-0.875}\text{ cm.}$

Plots of A against $\log w$, using Fowle's and Adel's results, gave curves for 7.25 , 7.5 , 7.75 and 8μ which were almost identical in form. Using different units for w at the four wavelengths, the experimental points can be made to cluster round a single curve. They are shown in fig. 2 clustered round a curve (curve V.) whose theoretical derivation is described below (§ 4).

These experimental results, like those for the Ψ' band, are open to the objection that they refer, for large w , to transmission of sunlight through the atmosphere, whose pressure and temperature are non-uniform.

where w_0 is the value of w for which absorption is half complete. This is illustrated in fig. 3, curve IX. The formula gives only a moderate representation of Fowle's data for Ψ' , and those of Fowle and Adel for $7.25-8\mu$; it indicates too rapid a variation of A with w below $A=50$ per cent, and too slow a variation above $A=80$ per cent. None the less, its simplicity makes it convenient for use in approximate work.

(ii) Elsasser (1938) derived a formula for the variation of A with w , assuming that the absorption lines are equal and evenly spaced, and that the absorption in each case is given by the Lorentz formula

$$k_\nu = k\gamma\pi^{-1}/\{(\nu-\nu_0)^2 + \gamma^2\}. \quad (2)$$

He found that, when absorption is complete at the line centres,

$$A = \text{erf}(\delta^{-1}(\gamma kw\pi)^{\frac{1}{2}}), \quad (3)$$

where δ is the frequency-spacing between the lines. This formula is illustrated in fig. 3, curve X. When w is so small that absorption is incomplete at the line centres, the error-function law ceases to be applicable; it asserts that $A \propto w^{\frac{1}{2}}$ when w is small, whereas in fact $A \propto w$ then.

Comparison with the experimental results of Fowle and Adel not only confirms the inapplicability of the formula (3) for small w ; it also shows that the error-function law gives too rapid an increase of A with w when $A > 50$ per cent. The reason is to be found in the irregularity in strength and spacing of the absorption lines, which permits the existence of certain wide gaps between the stronger lines. Such gaps being relatively transparent, a much greater increase in w is needed to increase the total absorption from a low value to a high than would be required if the lines were regularly distributed.

(iii) Schnaidt (1939) determined the variation of A with w numerically, making assumptions similar to Elsasser's. A complete blackout of the line-centres was not assumed, so that Schnaidt's results for small absorptions effectively complete Elsasser's. Instead of considering the lines as overlapping, Schnaidt supposed each to be cut off at a distance from the line-centre equal to five times the line-width 2γ , the next line beginning there. This assumption is, of course, unjustified; but the resultant increase in transparency between the lines is much the same as would result from occasional wide gaps between the lines. In fact, Schnaidt's absorption curve (fig. 3, curve XI.) is very like Fowle's curve for Ψ' over the whole range of A .

§ 4. To test more exactly the effect of the irregularity of the lines, and of the incompleteness of absorption at the line-centres, I have determined numerically the law of variation of A with w for various ranges in the rotation band. The Lorentz formula (2) was assumed, and calculations were made with a line-width $2\gamma = 0.4 \text{ cm.}^{-1}$ in the ranges 100–125, 225–250, 175–200, 200–225, 300–325 and 325–350 cm.^{-1} ; also with line-widths of 0.8, 0.2 and 0.1 cm.^{-1} for the first two ranges. The strengths and

positions of the absorption lines were taken from the work of Randall, Dennison, Ginsberg and Weber (1937). The calculations were mainly done in 1943; had they been done more recently, smaller line-widths might have been used, and the strengths of absorption lines might have been varied to accord with the work of Cross, Hainer and King (1944). However, the similarity between the results from the different ranges, in which the distribution of line-strengths was very different, indicated that a moderate variation in line-strengths cannot seriously affect the absorption curves.

In the calculations with $2\gamma=0.4\text{ cm.}^{-1}$, the total absorption coefficient from all neighbouring lines was first found at intervals of 0.2 cm.^{-1} throughout the range under consideration. The next step was to find the fractions of the range for which the logarithm (to base 10) of the absorption coefficient lay in each of successive ranges of magnitude 0.05. The contribution to the total absorption from these fractions were then determined for values of $\log_{10} w$ at intervals of 0.25, and were summed. Similar methods, with a different frequency-spacing, were used for the other line-widths.

The results for $2\gamma=0.4, 0.2$ and 0.1 cm.^{-1} are shown in fig. 1 (curves II., III., IV.) for the range $100\text{--}125\text{ cm.}^{-1}$, and in fig. 2 (curves V., VI., VII.) for $225\text{--}250\text{ cm.}^{-1}$. The second set of curves shows a slower increase of A with w than the first; this is due to the wide gap containing no absorption lines between 223.4 and 244.5 cm.^{-1} , which gives appreciable absorption only when w is large. Gaps like this, though usually less wide, occur frequently as the wing of the band is approached. The absorption curves consequently tend to show a decrease in steepness as the wave-number increases, though the curve for $225\text{--}250\text{ cm.}^{-1}$ actually represents an extreme form of band-wing absorption; the curves for $175\text{--}200$ and $200\text{--}225\text{ cm.}^{-1}$ have practically the same shape as that for $100\text{--}125\text{ cm.}^{-1}$, while those for $300\text{--}325$ and $325\text{--}350\text{ cm.}^{-1}$ have shapes intermediate between this and that for $225\text{--}250\text{ cm.}^{-1}$. A reduction in the line-width also leads to a decreased slope of the absorption curve.

Curves I. and II. of fig. 1 are very similar in shape. This is satisfactory, for it provides a direct experimental check on the theoretical curves. Cornell (1937) found mean line-widths 0.57 and 0.4 cm.^{-1} for the ρ and Φ bands respectively; thus the line-width in the Ψ' band is also probably about 0.4 cm.^{-1} . Hence if the distribution of strong and weak lines has the same random characteristics in the Ψ' and rotation bands, the absorption curves for the two should be much the same. The fact that this is indeed so is a striking confirmation of the validity of the Lorentz formula (2), used in the calculations.

The experimental results for $7.25\text{--}8\mu$ are shown in fig. 2 clustering closely round curve V. The agreement with this curve supplies a further experimental check on theory. The experimental results, like the theoretical curve, represent band-wing absorption (7.25μ is about 215 cm.^{-1}

from the centre of the 6.3μ band). The closeness of agreement between the two suggests that the line-width in the 6.3μ band is not very different from 0.4 cm.^{-1} , but little weight can be attached to this suggestion; one would obtain a similar absorption curve, assuming a less extreme band-wing absorption but a smaller line-width.

The line-width at the wing of the rotation band was found by Adel (1947) to be $0.22\text{--}0.24\text{ cm.}^{-1}$. There is no essential reason why the line-width should remain the same right down to very low wave-numbers, but observations at centimetre wave-lengths actually show a line-width which is similar in order of magnitude, though a little smaller (Becker and Autler 1946). Taking a uniform line-width $2\gamma=0.24\text{ cm.}^{-1}$, the numerical calculations just described can be used to estimate the actual absorption in various parts of the rotation band, as well as the run of the absorption curve. A comparison of the calculated absorptions with such scanty experimental data as exist provides a further check on theory.

In the range $100\text{--}125\text{ cm.}^{-1}$, Wright and Randall (1933) give transmission curves for 80 cm. of damp air, from which I estimate an absorption of roughly 55 per cent. The humidity is not quoted, but the quantity of absorbing water may be estimated as $(7\pm 2)\times 10^{-5}\text{ cm.}$; for this, the calculated absorption is 50 ± 6 per cent. In the ranges $300\text{--}325$ and $325\text{--}350\text{ cm.}^{-1}$, Hettner (1918) found $2.5\times 10^{-3}\text{ cm.}$ of precipitable water to give 52 per cent and 49 per cent absorption respectively. This was at 354° K. ; I estimate that $2.5\times 10^{-3}\text{ cm.}$ at this temperature should produce the same absorption, in the two ranges, as about 3×10^{-3} and $3.4\times 10^{-3}\text{ cm.}$ at room temperature. The theoretical absorptions of these amounts of water are 45 per cent and 43 per cent. In the ranges $200\text{--}225$ and $175\text{--}200\text{ cm.}^{-1}$, Kühne (1933) found 77 per cent and 69 per cent absorption to be produced by about $3.3\times 10^{-3}\text{ cm.}$ of water. The corresponding theoretical absorptions are 84 per cent and 78 per cent.

In view of the uncertainties, these figures show fair agreement between theory and experiment. The theory is admittedly approximate: the line-strengths are somewhat uncertain, particularly in the band-wing, where centrifugal stretching of the molecules may be important. Nevertheless, a comparison between curve VIII. of fig. 2 and the other curves of this figure indicates no reason to believe that the shape of the absorption curve at the extreme wing of the band is different from that at greater wavelengths.

It appears, then, that a single absorption curve can be used for regions near a band-centre, and a second for band-wings; because of possible differences in line-width, different curves should be used for the 6.3μ and rotation bands. However, in atmospheric work complication is avoided, and remarkably little error is involved, if a single absorption curve is used at all wavelengths. Such a curve is shown in fig. 3 (curve XII.); the material from which it is constructed is given in Table I. The table is based on the curves of figs. 1 and 2, adopting a line-width rather above $2\gamma=0.25\text{ cm.}^{-1}$, and a type of absorption approximating

more closely to the band-centre absorption of fig. 1 than to the rather extreme band-wing absorption of fig. 2. Tables are also given for line-widths one-half and one-quarter as large, corresponding to pressures of one-half and one-quarter of an atmosphere.

TABLE I.
Percentage absorption for given $\log_{10} (w/w_0)$,
at pressures of 1, $\frac{1}{2}$ and $\frac{1}{4}$ atmosphere.

$\log_{10} (w/w_0)$	Absorption			$\log_{10} (w/w_0)$	Absorption		
	1 atm.	$\frac{1}{2}$ atm.	$\frac{1}{4}$ atm.		1 atm.	$\frac{1}{2}$ atm.	$\frac{1}{4}$ atm.
-0.2	42	$42\frac{1}{2}$	$43\frac{1}{2}$	0.2	$58\frac{1}{2}$	58	$57\frac{1}{2}$
-0.4	34	$35\frac{1}{2}$	$36\frac{1}{2}$	0.4	67	66	65
-0.6	27	29	$30\frac{1}{2}$	0.6	75	$73\frac{1}{2}$	$72\frac{1}{2}$
-0.8	$20\frac{1}{2}$	22	23	0.8	$82\frac{1}{2}$	81	$79\frac{1}{2}$
-1.0	$15\frac{1}{2}$	$17\frac{1}{2}$	19	1.0	88	$86\frac{1}{2}$	85
-1.2	$11\frac{1}{2}$	$13\frac{1}{2}$	$14\frac{1}{2}$	1.2	$93\frac{1}{2}$	92	91
-1.6	$5\frac{1}{2}$	$7\frac{1}{2}$	$8\frac{1}{2}$	1.4	97	96	95
-2.0	$2\frac{1}{2}$	4	$5\frac{1}{2}$	1.6	99	$98\frac{1}{2}$	98
-2.4	1	2	3	1.8	100	100	$99\frac{1}{2}$

TABLE II.

Values of w_0 , for which absorption is half complete, at room temperature and at 220° K. (w_0 in cm. precipitable water).

Range	$\log_{10} w_0$		Range	$\log_{10} w_0$	
	Room temperature	220°		Room temperature	220°
5.0-5.2 μ	-1.3	-1.15	8-13 μ	0.6	0.85?
5.2-5.4	-1.6	-1.55	13-15	0.0?	0.3 ?
5.4-5.6	-1.9	-1.9	15-17	-0.5?	0.0 ?
5.6-5.8	-2.35	-2.35	17-19	-1.0	-0.35
5.8-6.05	-2.6	-2.65	19-21	-1.4	-0.9
6.05-6.2	-2.3	-2.35	21-23	-1.75	-1.3
6.2-6.35	-1.95	-2.0	23-25	-2.0	-1.6
6.35-6.45	-2.5	-2.55	25-27	-2.2	-1.85
6.45-6.7	-2.65	-2.7	27-30	-2.4	-2.15
6.7-6.9	-2.2	-2.2	30-34	-2.6	-2.45
6.9-7.2	-1.85	-1.85	34-40	-2.8	-2.7
7.2-7.4	-1.45	-1.4	40-50	-3.0	-3.0
7.4-7.6	-1.05	-0.95	50- ∞	-3.1	-3.15
7.6-7.8	-0.6	-0.4			
7.8-8.0	-0.15	0.1			

Table I. gives A for various values of $\log_{10} (w/w_0)$, where w_0 is, as before, the value of w for which A is 50 per cent. It needs to be supplemented by a further table giving w_0 for different wavelength ranges; this is given, for a pressure of one atmosphere, in Table II., columns (2) and (5).

The experimental work on which this table is based is, in general, that used in constructing Table II. of the earlier report (Cowling 1943); beyond 34μ , however, the numerical calculations described above have been used, and the residual ray observations of Strong and Woo (1932) have been disregarded. In the range $8\text{--}13\mu$, though values of w_0 are given, the absorption may approximate more closely to continuous absorption than to the kind of band absorption to which Table I. applies. The curves of figs. 1 and 2 enable one to estimate that the values of $\log_{10} w_0$ at pressures of $\frac{1}{2}$ and $\frac{1}{4}$ atmos. respectively are 0.25 and 0.51 greater than those at atmospheric pressure.

§ 5. *Pressure effects.* In the above it has been assumed, in accordance with the Lorentz theory of collision-broadening, that a reduction in pressure leads to a reduction in line-width in the same ratio. The Lorentz theory is usually accepted as valid for the infra-red absorption of gases (see, *e. g.*, Coggeshall and Saier 1947). Nevertheless, some workers have doubted its applicability to water vapour absorption, for the following reasons.

The absorption of water vapour, when between about 10 per cent and 50 per cent complete, approximately obeys the square-root law $A \propto w^{\frac{1}{2}}$ (see, *e. g.*, Strong 1941). This law can be given a theoretical justification, if the Lorentz formula (2) is assumed to be obeyed, and the amount of water present is supposed to be enough to black out the centres of absorption lines, but insufficient to produce much absorption in their overlapping wings. Making these assumptions, it is found that

$$A = 2\delta^{-1}w^{\frac{1}{2}}\Sigma(\gamma k)^{\frac{1}{2}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where δ is the frequency-range considered, and the summation is over all lines whose centres are in the range. Since γ is, on the collision-broadening theory, proportional to the pressure p , (4) implies that $A \propto p^{\frac{1}{2}}$; that is, a reduction in p produces the same decrease in A as a reduction in w in the same ratio. However, experiments show that, even for values of w such that $A \propto w^{\frac{1}{2}}$, A varies much more slowly than $p^{\frac{1}{2}}$. Falckenberg (1938) found that the effect on the total absorption, integrated over all wavelengths, of a k -fold decrease in p , is roughly equivalent to that of reducing w in the ratio $k^{\frac{1}{2}}$; Schnaidt (1939) obtained a similar result from v. Bahr's (1909) experimental results for absorption near 2.7μ . Though their results referred to a very limited range of variation of w , this law of pressure variation of the absorption has often been taken as generally valid, and has been interpreted as implying that the line-width is not proportional to the pressure itself, but to its square root.

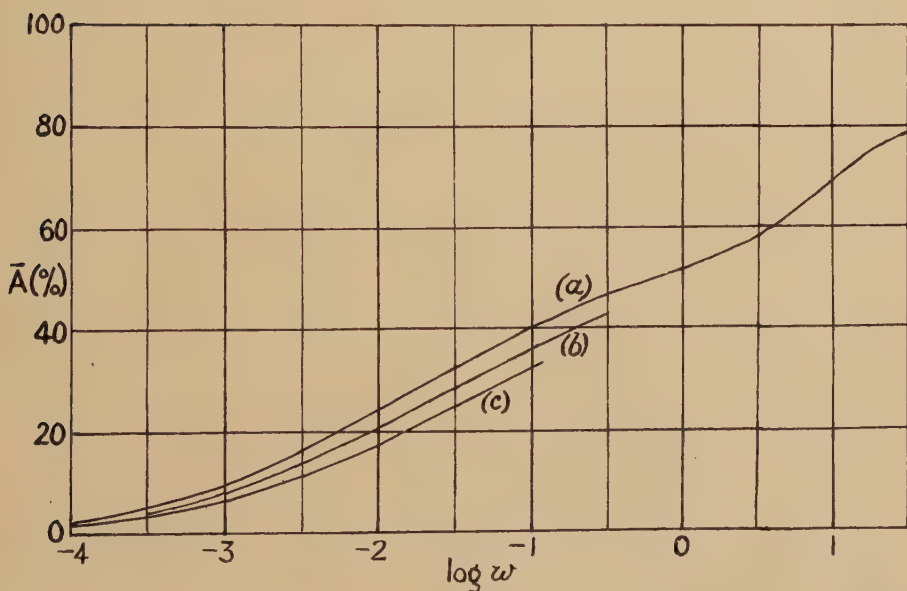
But it is not actually necessary to abandon the Lorentz theory. The numerical work described in the last section enables one to see whence the apparent contradiction has arisen. It shows that there are no very secure theoretical grounds for using the formula (4). No range of values of w exists such that the absorption at line-centres is complete, and that in the region of overlapping wings weak; the wings of strong lines begin

15 per cent in the more opaque wavelengths.) A four-fold reduction in pressure is equivalent to replacing w by $\frac{2}{3}w$ when $\bar{A}=2$ per cent, by $\frac{1}{2}w$ when $\bar{A}=9$ per cent, and by $\frac{1}{3}w$ when $\bar{A}=40$ per cent. The calculated values for $w=1.2 \times 10^{-3}$ and 2.4×10^3 cm. are compared with Falckenberg's (1938) experimental values in Table III. The two sets of values indicate

TABLE III.
Calculated integral absorptions,
compared with Falckenberg's observed values.

	$w=1.2 \times 10^{-3}$ cm.		$w=2.4 \times 10^{-3}$ cm.	
	$\bar{A}$ (obs.) (per cent)	$\bar{A}$ (calc.) (per cent)	$\bar{A}$ (obs.) (per cent)	$\bar{A}$ (calc.) (per cent)
1 atm.	7.8	10.8	12.4	14.6
$\frac{1}{2}$ atm.	6.4	8.7	—	—
$\frac{1}{4}$ atm.	4.5	6.9	8.4	9.6

Fig. 4.



Graphs of integral absorption $\bar{A}$ against $\log w$ (w measured in cm.) at pressures of 1 (curve (a)), $\frac{1}{2}$ (curve (b)), and $\frac{1}{4}$ (curve (c)) atmosphere.

pressure changes in the absorption in roughly the same ratio. The actual values of the experimental absorption do not agree at all closely with theory, but this is not surprising. The experimental results refer to absorption of radiation from a source at $100^\circ\text{C}.$; as Schnaidt (1938) pointed out, they need to be corrected by increasing them by about 30 per cent; and if they are corrected thus, the values at 1 atmos. are definitely higher than those found by other workers.

The calculated values of $\bar{A}$ at the different pressures are shown in fig. 4. Absorption in the ranges $0-5\mu$ and $13-17\mu$ is omitted, since in the atmosphere water-vapour absorption in these ranges is dominated by that of CO_2 ; this facilitates a comparison with experiments made with atmospheric air and corrected by subtracting the estimated CO_2 absorption. For small values of w (less than $10^{-2.5}$ cm.) the calculated $\bar{A}$ at atmospheric pressure is about one-sixth less than the emissivity found by Falckenberg (1939), and about the same amount greater than that found by Elsasser (1941); it agrees fairly closely with that found by Brooks (1941). For large values of w (greater than 1 mm.) the calculated $\bar{A}$ is less than Elsasser's by two or three per cent of the black-body radiation, and a similar amount less than of Brooks: it exceeds by a rather smaller amount that of Robinson (1947), derived from what he calls observations of minimum radiation, but agrees with the mean of Robinson's observations, including those which he regards as subject to extraneous radiation. In view of the uncertainties the agreement of the calculated absorptions with experiment is satisfactory.

§ 7. *Atmospheric pressures effects.* By reason of the non-uniformity of pressure the problem of pressure corrections to atmospheric absorption is more subtle than the corresponding problem when the whole absorbing column is at the same pressure. Consider, for example, absorption of radiation leaving the earth's surface in a given direction and traversing the whole atmosphere. The pressure correction to the part of the absorption which takes place in the upper atmosphere has to be applied to an *increment* to the absorption. At different pressures the separate wavelengths of a range contribute slightly different amounts to a total absorption A of assigned amount in that range. Ignoring this difference, which is probably unimportant save for very small values of A , the pressure correction to an increment of A is equivalent to reducing the amount of water vapour in the ratio $(dA/dw)_p : (dA/dw)_a$, where $(dA/dw)_a$ is the value of dA/dw at atmospheric pressure and $(dA/dw)_p$ is that at the pressure concerned. The value of the ratio depends on A , the absorption in layers below that considered. A similar correction has to be applied in considering radiation reaching the ground surface from the upper atmosphere.

Values of the ratio, deduced from the data of figs. 1 and 2, are given in Table IV. It will be noted that the pressure correction is greater than reducing the quantity of water vapour in the same ratio as $p^{1/2}$; save for very small absorptions the reduction is more nearly in the same ratio as p . Table IV. also contains values of $(d\bar{A}/dw)_p : (d\bar{A}/dw)_a$, giving the similar reduction in the effective water amount in considering the integral absorption; the values of this ratio vary less with the total absorption than do those of the first ratio.

§ 8. *Temperature effects.* A variation in the temperature T affects the absorption in two ways. At given pressure, the line-width varies like $T^{-7/10}$. Temperature changes also affect the populations of the different

energy-levels; the high-energy levels, which contribute most to band-wing absorption, are but scantily occupied at low temperatures. A decrease in temperature therefore leads to an increase in absorption near a band centre (for the rotation band at great wavelengths) but makes the absorption cut-off at the wings of the band sharper.

The only genuinely reliable theoretical method of estimating the absorption at low temperatures would be by carrying out calculations like those described in § 4, for each of a series of wavelength ranges. A less complicated approximate method has, however, been used. The intensities of lines in the rotation band between 75 and 550 cm^{-1} were first calculated for a variety of temperatures. As the temperature falls off, weak lines are found to be reduced in strength more than the strong ones; thus the gaps between strong lines tend to be more accentuated and the absorption tends to possess more of the characteristics of band-wing absorption. The effect is not large, however, and is offset by the increased line-width; hence it is reasonable to take A to vary with w according to Table I., as at ordinary temperatures. Then, to determine the absorption at any wavelength, it is necessary only to know w_0 .

TABLE IV.

Values of $(dA/dw)_p/(dA/dw)_a$ and $(d\bar{A}/dw)_p/(d\bar{A}/dw)_a$, corresponding to $p=\frac{1}{2}$ and $\frac{1}{4}$ atmosphere.

$\left(\frac{dA}{dw}\right)_p : \left(\frac{dA}{dw}\right)_a$			$\left(\frac{d\bar{A}}{dw}\right)_p : \left(\frac{d\bar{A}}{dw}\right)_a$		
A	$\frac{1}{2}$ atm.	$\frac{1}{4}$ atm.	$\bar{A}$	$\frac{1}{2}$ atm.	$\frac{1}{4}$ atm.
(per cent)			(per cent)		
5	0.82	0.6	5	0.7	0.44
10	0.72	0.46	10	0.65	0.39
15	0.67	0.4	15	0.62	0.36
20	0.64	0.36	20	0.60	0.34
30	0.60	0.33	25	0.58	0.33
40	0.57	0.3	30	0.56	0.31
50	0.54	0.28	35	0.55	0.30
60	0.52	0.265	40	0.55	—
80	0.5	0.25			

To determine w_0 the formula (4) is used. This formula indicates 19 per cent absorption when the true absorption is about $15\frac{1}{2}$ per cent. Hence w_0 is about ten times the value of w which (4) indicates to give 19 per cent absorption.

In using (4) one is, of course, only following Elsasser (1938), who calculated the coefficient of $w^{\frac{1}{2}}$ in this formula for ranges 25 cm^{-1} broad between 75 and 550 cm^{-1} , at temperatures between 200 and 320° K. As noted in my earlier report, Elsasser's calculations were subject to systematic errors; my own results agree with his (as regards order of magnitude) between 75 and 375 cm^{-1} , but give values of w_0 only

one-hundredth as large as his in the range $475\text{--}550\text{ cm.}^{-1}$. Nevertheless, my results differ little from his in the ratios which they give for the values of w_0 at different temperatures for any given wavelength range, and it is therefore unnecessary to give my results in detail. They indicate that, for wavelengths greater than 50μ , the absorption at 220° K. is slightly greater than that at room temperature: in the range $40\text{--}50\mu$ the absorptions at the two temperatures are roughly the same; while for shorter wavelengths the absorption at 200° K. becomes progressively the smaller of the two, until near 20μ the value of w_0 at 220° K. is about five times that at room temperature. The estimate at 20μ cannot be regarded as very reliable; the estimated value of w_0 at room temperature here is at least twice that indicated by experiment. However, the calculated ratios of w_0 at room temperature and at 200° K. have been used to construct a table for w_0 at 220° K. ; this is given in Table II., third and sixth columns. The temperature variation at a frequency ν in the 6.3μ band is taken to be roughly that at a frequency $|\nu - \nu_0|$ in the rotation band, where ν_0 is the frequency of the 6.3μ band centre.

TABLE V.

Values of $\bar{A}(a)$ at 220° K. and $\frac{1}{4}\text{ atm.}$, compared with (b) values uncorrected for the change of absorption with temperature, and (c) values at room temperature and pressure $\frac{1}{4}\text{ atm.}$

$w(\text{cm.})$	10^{-4}	$10^{-3.5}$	10^{-3}	$10^{-2.5}$	10^{-2}	$10^{-1.5}$	10^{-1}
percentage $\bar{A}(a)$	2.3	4.5	8.2	13.6	20.65	28.9	37.4
percentage $\bar{A}(b)$	2.6	5.3	9.7	16.0	24.2	33.7	43.0
percentage $\bar{A}(c)$	1.7	3.4	6.4	11.1	17.2	24.8	32.5

The temperature variation in w_0 is large only in the relatively transparent band wings. In the upper atmosphere, where the total amount of absorbing vapour is small, its effect on the integral absorption $\bar{A}$ is masked by the increasing importance, at low temperatures, of long wavelengths, where water vapour absorbs strongly. Table V. gives the calculated integral absorption at 220° K. of black-body radiation at this temperature, both when account is taken of the temperature variation of w_0 , and when the values of w_0 appropriate to room temperature are used uncorrected. The calculations refer in each case to a pressure of $\frac{1}{4}\text{ atmos.}$; the corresponding integral absorptions at room temperature are also given for comparison. The increase in $\bar{A}$ due to the increased importance of long wavelengths at low temperatures is about twice the decrease due to the increased transparency of the band-wings.

§ 9. *Conclusion.* In discussing the absorption of long-wave radiation in the atmosphere, drastic simplifying approximations are often necessary. It is hoped that the data given in this paper will enable the value of such approximations to be assessed. For example, the pressure correction

which replaces a quantity w of water vapour at pressure p by a quantity $w\sqrt{(p/p_a)}$ at atmospheric pressure p_a is in most cases an undercorrection ; the true correction is often nearer to replacing w by $w p/p_a$.

However, it must be emphasized that the approximations justified in any particular problem must depend on that problem. As noted in the last section, the emissivity of a small quantity of water vapour, measured as a fraction of the black-body radiation, increases with decreasing temperature. But the radiation reaching the ground from great heights does not mirror this increased emissivity. The radiation emitted by water at great heights is chiefly emitted in very long wavelengths, which are subject to great absorption in the lower levels. On the other hand, in considering the radiative equilibrium of the stratosphere the increased emissivity at low temperatures should be important.

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*X. Orthogonal Polynomials in the Least Squares
Fitting of Observations.*

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SUMMARY.

The theory of least squares curve-fitting of non-equidistant data is developed in terms of orthogonal polynomials and power moments. A modification of the Doolittle scheme is proposed which enables probable error calculations to be carried out very simply. The modified scheme is illustrated by a specific example.

§ 1. INTRODUCTION.

IN recent years the use of orthogonal polynomials in the fitting of curves to equally-spaced observations has been thoroughly investigated by a number of authors (Birge and Shea 1927, Aitken 1932, Davis 1935, Kerawala 1941, Fisher 1946, Birge 1947). A comprehensive discussion of these investigations has been given by Birge (1947).

When the observations are not made at equally-spaced intervals, the special methods of these authors are no longer applicable. In these general cases it is necessary to solve the normal equations algebraically. The usual method employed is that of Doolittle (1878). In the Doolittle method the calculation of the power-series coefficients is quite straightforward, but the probable error calculations (Brunt 1917) are somewhat involved.

Probable error calculations are greatly simplified by the use of orthogonal polynomials. Fisher (1946) states that the method of orthogonal polynomials becomes artificial in the general case where the observations are not equally spaced. This is true in the sense that the calculation of the orthogonal polynomials $T_j(x)$ at each point of observation for use in the orthogonal moments $\sum y T_j(x)$ would require an exorbitant amount of time. In fact, as Aitken (1933-34) points out, the only practicable method is to base the calculations on the power moments $\sum y x^j$.

Although the direct calculation of orthogonal polynomials and orthogonal moments is out of the question, it is highly desirable that the fitted curve should be expressed in orthogonal as well as in power-series form. The advantages of orthogonal representation are:—

(i) All curves of degree less than p are obtained in the process of obtaining the curve of degree p .

(ii) The probable error calculations for the power-series coefficients and for the fitted values are greatly simplified.

* Communicated by the Author.

The purpose of the present paper is to develop the general theory of curve-fitting in terms of orthogonal polynomials and power moments. By this means the advantages of the orthogonal method of solution are obtained without the prohibitive labour of calculating directly the orthogonal moments.

It is found that the arithmetical procedure is very closely related to that of the Doolittle scheme. The various terms in the Doolittle scheme are shown to be identical with terms appearing in the expansion of the orthogonal polynomials. The values $S_{jj}(=\Sigma T_j^2(x))$ and β_{jk} (identical with Birge's R_{jk}) which form the basis of the probable error calculations may in fact be calculated from terms which appear in the Doolittle scheme.

A variation of the Doolittle scheme is proposed which makes use of the advantage arising from orthogonal representation. The scheme is extended to include the calculation of probable errors both of the power-series coefficients and the fitted values.

Aitken (1932-34) in a series of three papers has given a comprehensive treatment of the problem of curve-fitting. In the second of these papers he develops a general scheme applicable to the case of non-equidistant data. It is doubtful whether Aitken's scheme would be of very great practical use except where the values Σx^j are fairly small. The scheme, unlike that of Doolittle, calculates the coefficients β_{jk} , and so can be extended to include probable error calculations. It is considered briefly in §2.

Tchebycheff originally obtained his polynomials in the form of continued fractions. Isserlis (1927) has discussed the problem of curve-fitting by means of Tchebycheff polynomials expressed in this form. Though interesting from a mathematical viewpoint, his scheme is too involved to yield a satisfactory practical procedure.

§ 2. GENERAL THEORY.

Let $y(x_i)$, $i=1, 2, \dots, n$, represent the n observations which are to be fitted to a polynomial of degree p in x , the errors in the observed values of the variable x being supposed negligible. The polynomial $u_p(x)$ to fit these observations is to be chosen so that the sum of the squares of the residuals $y(x_i)-u(x_i)$ should be a minimum.

(a) *Calculation of Tchebycheff Polynomials.*

The polynomial $u_p(x)$ will be expanded in terms of polynomials $T_j(x)$ of degree $j=0$ to p , which are orthogonal over the particular set of values x_i at which the observations were made. The polynomials $T_j(x)$ are the orthogonal polynomials of Tchebycheff, satisfying the equations

$$\sum_{i=1}^n T_j(x_i)T_k(x_i)=0, \quad j \neq k. \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The equations (1) determine the polynomials $T_j(x)$ except for a single arbitrary constant in each polynomial. This constant is accounted for

by imposing the additional condition that the coefficient of the leading term x^j in the power-series expansion of $T_j(x)$ should be unity.

In order to derive an explicit expression for the polynomial $T_j(x)$, it is written as a linear function of the polynomials of lower degree.

$$T_j(x) = x^j + \alpha_{j,j-1}T_{j-1}(x) + \alpha_{j,j-2}T_{j-2}(x) + \dots + \alpha_{j0} \quad (2)$$

To find the coefficient α_{jk} , (2) is multiplied by $T_k(x)$ and summed over the values x_i . Thus

$$\Sigma T_j(x)T_k(x) = \Sigma x^j T_k(x) + \alpha_{jk} \Sigma T_k^2(x) = 0$$

and

$$\alpha_{jk} = -\Sigma x^j T_k(x) / \Sigma T_k^2(x).$$

This can be written as

$$\alpha_{jk} = -S_{jk}/S_{kk}, \quad (3)$$

where

$$\left. \begin{aligned} S_{jk} &= \Sigma x^j T_k(x), \\ S_{kk} &= \Sigma x^k T_k(x) \equiv \Sigma T_k^2(x). \end{aligned} \right\} \quad (4)$$

Now

$$\begin{aligned} S_{jk} &= \Sigma x^j T_k(x) \\ &= \Sigma x^j (x^k + \alpha_{k,k-1}T_{k-1}(x) + \dots + \alpha_{k0}) \\ &= S_{j+k,0} + \alpha_{k,k-1}S_{j,k-1} + \dots + \alpha_{k0}S_{j0}. \end{aligned} \quad (5)$$

The values of S_{jk} and α_{jk} can then be calculated in succession from the sums of the powers $S_{j+k,0}$ and the previously calculated values S_{jm} and α_{km} ($m < k$).

To express $T_j(x)$ as a power series

$$T_j(x) = x^j + \beta_{j,j-1}x^{j-1} + \dots + \beta_{j0}, \quad (6)$$

the coefficients β_{jk} are determined by expanding each term on the right-hand side of (2) in powers of x and collecting terms in x^k . Thus

$$\beta_{jk} = \alpha_{jk} + \alpha_{j,j+1}\beta_{k+1,k} + \alpha_{j,j+2}\beta_{k+2,k} + \dots + \alpha_{j,j-1}\beta_{j-1,k}, \quad (7)$$

and the coefficients $\beta_{k+1,k}$, $\beta_{k+2,k}$, ... can be built up in successive steps.

(b) Coefficients of the Polynomial of Best Fit.

The polynomial $u_p(x)$ is written in the form

$$u_p(x) = a_p T_p(x) + a_{p-1} T_{p-1}(x) + \dots + a_1 T_1(x) + a_0, \quad (8)$$

where the coefficients a_j are to be chosen so that the expression

$$\Sigma v_p^2(x_i) = \Sigma \{y(x_i) - u_p(x_i)\}^2 \quad (9)$$

is a minimum. Differentiating the right-hand expression with respect to a_j to obtain the normal equations,

$$\Sigma\{y(x_i)-u_p(x_i)\}T_j(x_i)=0. \quad . \quad . \quad . \quad . \quad . \quad (10)$$

Then

$$\Sigma y(x)T_j(x)=a_j\Sigma T_j^2(x)$$

or

$$a_j=\Sigma y(x)T_j(x)/\Sigma T_j^2(x). \quad . \quad . \quad . \quad . \quad . \quad (11)$$

The power moments M_j of the observations are defined in the usual way :

$$M_j=\Sigma x^j y(x). \quad . \quad . \quad . \quad . \quad . \quad (12)$$

The orthogonal moments M'_j are defined by the equations

$$M'_j=\Sigma T_j(x)y(x). \quad . \quad . \quad . \quad . \quad . \quad (13)$$

The equation for a_j may then be written in the form

$$a_j=M'_j/S_{jj}. \quad . \quad . \quad . \quad . \quad . \quad (14)$$

Now $T_j(x)$ in (13) can be expanded by using either (2) or (6). We obtain respectively

$$\begin{aligned} a_j &= \Sigma y(x)\{x^j + \alpha_{j,j-1}T_{j-1}(x) + \dots + \alpha_{j0}\}/S_{jj} \\ &= \{M_j + \alpha_{j,j-1}M'_{j-1} + \alpha_{j,j-2}M'_{j-2} + \dots + \alpha_{j0}M'_0\}/S_{jj} \end{aligned} \quad . \quad (15)$$

and

$$\begin{aligned} a_j &= \Sigma y(x)\{x^j + \beta_{j,j-1}x^{j-1} + \dots + \beta_{j0}\}/S_{jj} \\ &= \{M_j + \beta_{j,j-1}M_{j-1} + \beta_{j,j-2}M_{j-2} + \dots + \beta_{j0}M_0\}/S_{jj}. \end{aligned} \quad . \quad (16)$$

Either of the equations (15) and (16) can be used to calculate a_j .

The polynomial of best fit is most commonly required in the form of a power series in x ,

$$u_p(x) = b_{pp}x^p + b_{p,p-1}x^{p-1} + \dots + b_{p0}. \quad . \quad . \quad . \quad (17)$$

Substitution of the expressions $T_j(x)$ given by (6) in (8), and collection of terms in x^j , leads to the equations

$$b_{pj} = a_j + \beta_{j+1,j}a_{j+1} + \beta_{j+2,j}a_{j+2} + \dots + \beta_{pj,p}. \quad . \quad . \quad (18)$$

An alternative expression is found by substitution of the values $\beta_{j,k}$ from equation (7) and grouping of terms in $a_{j,k}$.

$$\begin{aligned} b_{pj} &= a_j + \alpha_{j+1,j}(a_{j+1} + \beta_{j+2,j+1}a_{j+2} + \dots + \beta_{p,j+1}a_p) \\ &\quad + \alpha_{j+2,j}(a_{j+2} + \beta_{j+3,j+2}a_{j+3} + \dots + \beta_{p,j+2}a_p) + \dots \\ &= a_j + \alpha_{j+1,j}b_{p,j+1} + \alpha_{j+2,j}b_{p,j+2} + \dots + \alpha_{pj,p}b_{pp}. \end{aligned} \quad . \quad . \quad . \quad (19)$$

Either of the equations (18) and (19) can be used to calculate the coefficients b_{pj} .

If the power-series expansion of $u_p(x_i)$ is substituted in (10), the normal equations become

$$\Sigma\{y(x_i) - (b_{p0} + b_{p1}x + \dots + b_{pp}x^p)\}T_j(x) = 0$$

for all j in the range 0 to p . Using (2), the set of normal equations reduces to

$$\Sigma\{y(x_i) - (b_{p0} + b_{p1}x + \dots + b_{pp}x^p)\}x^j = 0$$

or

$$b_{p0}S_{j0} + b_{p1}S_{j+1,0} + \dots + b_{pp}S_{j+p,0} = M_j. \quad \dots \quad (20)$$

This is the form in which the normal equations are generally written.

Substitution of the calculated coefficients b in the equations (20) (for $j=0$ and 1, say) provides a check on the arithmetical calculations.

(c) *Practical Methods of Calculation.*

There are two possible ways of carrying out the calculations; the first using the coefficients α , the second the coefficients β . In each system the α_{jk} and the S_{jj} are calculated. In the first system (the α -system) the coefficients α are used directly, while in the second system (the β -system) the coefficients β are determined from the α and then used in the remainder of the calculations. The appropriate equations for a and b are (15) and (19) in the α -system, (16) and (18) in the β -system.

The α -system is essentially the familiar Gauss-Doolittle method of solving the normal equations. Table I. shows a typical Doolittle scheme (based on that of Goulden (1939)), with the entries in our notation.

The principal disadvantage of the α -system is that the terms $\alpha_{kj}b_{pk}$ in the expression for b_{pj} are different for polynomials of different degree p , and have to be calculated separately for each degree. In the β -system the terms $\beta_{kj}a_j$ in the expression for b_{pj} are the same for polynomials of different degree.

The coefficients β_{jk} are needed for probable error calculations, and so if probable errors are to be calculated it would seem best to evaluate the β_{jk} and use the β -system. If a number of different sets of observations are to be fitted, the values x_i being the same for each set, the β_{jk} can be calculated once and for all. It is also possible to calculate the a_j by the α -system (as in the Doolittle scheme), then the values β_{jk} , and finally the b_{pj} as in the β -system. The β -system is used in the illustrative example in § 4.

Aitken's scheme (1933-34 b) is essentially a variation of the β -system. The scheme is based on a method of solution of simultaneous equations developed by Aitken (1932). Since the scheme will hardly be understood without a knowledge of this method, a detailed account will not be given here. A feature of the scheme is that division is postponed throughout

the table; for example, the entry corresponding to $S_{21}=S_{30}+\alpha_{10}S_{20}$ is written as $S_{00}S_{30}-S_{10}S_{20}=S_{00}S_{21}$ and the number S_{00} is entered in a divisor column. There are no non-terminating decimals in the table, but the later entries become very large.

In our notation the entries in the top right-hand line of each section of Aitken's scheme are (when divided by the divisor) the coefficients β_{jk} . Thus, although Aitken does not himself carry out probable error calculations, the required values β_{jk} are displayed in his table. As in our β -system, all the polynomials of lower degree are obtained in the process of calculating a polynomial of given degree.

TABLE I.
The Doolittle Scheme.

1.	S_{00}	S_{10}	S_{20}	S_{30}	M_0
2. Divide by $-S_{00}$	α_{10}	α_{20}	α_{30}		$-a_0$
3.		S_{20}	S_{30}	S_{40}	M_1
4. $\alpha_{10} \times (1)$	$\alpha_{10}S_{10}$	$\alpha_{10}S_{20}$	$\alpha_{10}S_{30}$		$\alpha_{10}M_0$
5. Add	S_{11}	S_{21}	S_{31}		M'_1
6. Divide by $-S_{11}$		α_{21}	α_{31}		$-a_1$
7.		S_{40}	S_{50}	M_2	
8. $\alpha_{20} \times (1)$		$\alpha_{20}S_{20}$	$\alpha_{20}S_{30}$	$\alpha_{20}M_0$	
9. $\alpha_{21} \times (5)$		$\alpha_{21}S_{21}$	$\alpha_{21}S_{31}$	$\alpha_{21}M'_1$	
10. Add		S_{22}	S_{32}	M'_2	
11. Divide by $-S_{22}$			α_{32}	$-a_2$	
12.			S_{60}	M_3	
13. $\alpha_{30} \times (1)$			$\alpha_{30}S_{30}$	$\alpha_{30}M_0$	
14. $\alpha_{31} \times (5)$			$\alpha_{31}S_{31}$	$\alpha_{31}M'_1$	
15. $\alpha_{32} \times (10)$			$\alpha_{32}S_{32}$	$\alpha_{32}M'_2$	
16. Add			S_{33}	M_3	
17. Divide by $-S_{33}$				$-a_3$	
	$b_{33}=$				a_3
	$b_{32}=$			$\alpha_{32}b_{33}$	a_2
	$b_{31}=$		$\alpha_{21}b_{32}$	$\alpha_{31}b_{33}$	a_1
	$b_{30}=$	$\alpha_{10}b_{31}$	$\alpha_{20}b_{32}$	$\alpha_{30}b_{33}$	a_0

(d) Probable Errors.

The sum of the squares of the residuals is given by the equation

$$\begin{aligned}\Sigma v_p^2 &= \Sigma \{y(x_i) - \mu_p(x_i)\}^2 \\ &= \Sigma \{y(x_i) - a_0 - a_1 T_1(x_i) - \dots - a_p T_p(x_i)\}^2,\end{aligned}$$

and so, using (11),

$$\left. \begin{aligned}\Sigma v_p^2 &= \Sigma y^2 - S_{00}a_0^2 - S_{11}a_1^2 - \dots - S_{pp}a_p^2 \\ &= \Sigma y^2 - M'_0a_0 - M'_1a_1 - \dots - M'_pa_p \\ &= \Sigma y^2 - M_0'^2/S_{00} - M_1'^2/S_{11} - \dots - M_p'^2/S_{pp}.\end{aligned} \right\} \quad (21)$$

Σv_p^2 can also be obtained by calculating the various $u(x_i)$ directly. As a check on the arithmetical calculations it may be desirable to compute Σv_p^2 by both methods.

The probable error r_p of an observation $y(x_i)$ of unit weight is then given by the usual formula

$$r_p = 0.6745 \{ \Sigma v_p^2 / (n - p - 1) \}^{\frac{1}{2}}. \quad . \quad . \quad . \quad . \quad (22)$$

To find the probable errors of the coefficients of $u_p(x)$, these coefficients must be expressed as explicit functions of the observations. Thus

$$a_k = \Sigma \{ T_k(x_i) / S_{kk} \} \cdot y(x_i),$$

and hence

$$\begin{aligned} r^2[a_k] &= \Sigma \left(\frac{\partial a_k}{\partial y(x_i)} \right)^2 r^2[y(x_i)] \\ &= r_p^2 / S_{kk}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (23) \end{aligned}$$

For the coefficients b_{pk} ,

$$r^2[b_{pk}] = \Sigma \left(\frac{\partial b_{pk}}{\partial y(x_i)} \right)^2 r^2[y(x_i)],$$

and, expanding b_{pk} as a function of the a_j using (18),

$$\begin{aligned} r^2[b_{pk}] &= r_p^2 \Sigma \{ T_k(x_i) / S_{kk} + \beta_{k+1, k} T_{k+1}(x_i) / S_{k+1, k+1} + \dots \}^2 \\ &= r_p^2 \{ 1 / S_{kk} + \beta_{k+1, k}^2 / S_{k+1, k+1} + \dots + \beta_{pk}^2 / S_{pp} \}, \quad . \quad . \quad . \quad (24) \end{aligned}$$

since the cross-products $\Sigma T_j(x) T_k(x)$ vanish.

Because the polynomials T_j, x are orthogonal, the coefficients a_j behave as independently observed quantities in probable error calculations. For example, formula (24) can be written

$$r^2[b_{pk}] = \sum_{j=k}^p \left(\frac{\partial b_{pk}}{\partial a_j} \right)^2 r^2[a_j]. \quad . \quad . \quad . \quad . \quad . \quad (25)$$

e) Fitted Values.

If the fitted values are required at various points x (which may or may not be members of the set x_i), they may be calculated by means of the power series (17). The probable errors of the fitted values at the points x are given by the equations

$$\begin{aligned} r^2[u_p(x)] &= r^2[a_0] + T_1^2(x) r^2[a_1] + T_2^2(x) r^2[a_2] + \dots \\ &= r_p^2 \{ 1 / S_{00} + T_1^2(x) / S_{11} + T_2^2(x) / S_{22} + \dots \} \\ &= r_p^2 \{ 1 / S_{00} + (x + \beta_{10})^2 / S_{11} + (x^2 + \beta_{21}x + \beta_{20})^2 / S_{22} + \dots \}. \quad . \quad (26) \end{aligned}$$

(f) *Changes of Origin and Scale.*

It is sometimes necessary to change the origin and scale of the variable x . Suppose it is desired to convert the polynomial $u_p(x)$ into a polynomial $u_p(\xi)$ in the new variable

$$\xi = (x + h)/m. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (27)$$

Then

$$\begin{aligned} u_p(\xi) &= b_{p0} + b_{p1}(m\xi - h) + b_{p2}(m\xi - h)^2 + \dots \\ &= c_{p0} + c_{p1}\xi + c_{p2}\xi^2 + \dots, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (28) \end{aligned}$$

where

$$c_{pj} = m^j \sum_{k=j}^p (-h)^{k-j} \binom{k}{j} b_{pk}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (29)$$

To calculate the probable errors it is necessary to express the coefficients as explicit functions of the a_k . Thus

$$c_{pj} = m^j \sum_{k=j}^p \gamma_{kj} a_k, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (30)$$

where

$$\gamma_{kj} = \sum_{q=j}^k (-h)^{q-j} \binom{q}{j} \beta_{kq}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (31)$$

and so

$$r[c_{pj}] = m^j \left(\sum_{k=j}^p \gamma_{kj}^2 / S_{kk} \right)^{\frac{1}{2}} r_p. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (32)$$

§ 3. TABLES OF SYMBOLS AND FORMULÆ.

(a) *Symbols.*

$y(x_i)$	observations.
$u_p(x)$	least squares polynomial of degree p which fits the $y(x_i)$.
$T_j(x)$	Chebyscheff polynomial of degree j .
S_{j0}	$\sum x^j$.
S_{jk}	$\sum x^j T_k(x)$.
α_{jk}	coefficient of $T_k(x)$ in orthogonal expansion of $T_j(x)$.
β_{jk}	coefficient of x^k in power-series expansion of $T_j(x)$.
M_j	$\sum x^j y(x)$, j th power moment of the observations.
M'_j	$\sum T_j(x) y(x)$, j th orthogonal moment of the observations.
a_j	coefficient of $T_j(x)$ in orthogonal expansion of $u_p(x)$.
b_{pj}	coefficient of x^j in power-series expansion of $u_p(x)$.
v_p	residual $y(x_i) - u_p(x_i)$.
r_p	probable error of an observation of unit weight.
$r[a_k]$	probable error of a_k .
$r[b_{kp}]$	probable error of b_{kp} .
$r[u_p(x)]$	probable error of fitted value $u_p(x)$.
ξ	$(x + h)/m$, change of variable.
c_{pj}	coefficient of ξ^j in power-series expansion of $u_p(\xi)$.

(b) *Formulæ.*

$$\begin{aligned}
S_{j0} &= \Sigma x^j. \\
S_{jk} &= S_{j+k,0} + \alpha_{k,k-1} S_{j,k-1} + \alpha_{k,k-2} S_{j,k-2} + \dots + \alpha_{k0} S_{j0}. \\
\alpha_{jk} &= -S_{jk}/S_{kk}. \\
\beta_{jk} &= \alpha_{jk} + \alpha_{j,k+1} \beta_{k+1,k} + \alpha_{j,k+2} \beta_{k+2,k} + \dots + \alpha_{j,j-1} \beta_{j-1,k}. \\
M_j &= \Sigma y x^j. \\
M'_j &= M_j + \beta_{j,j-1} M_{j-1} + \beta_{j,j-2} M_{j-2} + \dots + \beta_{j0} M_0. \\
&= M_j + \alpha_{j,j-1} M'_{j-1} + \alpha_{j,j-2} M'_{j-2} + \dots + \alpha_{j0} M'_0. \\
a_j &= M'_j/S_{jj}. \\
b_{pj} &= a_j + \beta_{j+1,j} a_{j+1} + \beta_{j+2,j} a_{j+2} + \dots + \beta_{pj} a_p. \\
&= a_j + \alpha_{j+1,j} b_{p,j+1} + \alpha_{j+2,j} b_{p,j+2} + \dots + \alpha_{pj} b_{pp}. \\
\Sigma v_p^2 &= \Sigma y^2 - S_{00} a_0^2 - S_{11} a_1^2 - \dots - S_{pp} a_p^2. \\
&= \Sigma y^2 - M'_0 a_0 - M'_1 a_1 - \dots - M'_p a_p. \\
&= \Sigma y^2 - M_0'^2/S_{00} - M_1'^2/S_{11} - \dots - M_p'^2/S_{pp}. \\
r_p &= 0.6745 \{ \Sigma v_p^2 / (n-p-1) \}^{\frac{1}{2}}. \\
r[b_{pj}] &= r_p (1/S_{jj} + \beta_{j+1,j}^2/S_{j+1,j+1} + \dots + \beta_{pj}^2/S_{pp})^{\frac{1}{2}}. \\
u_p(x) &= b_{p0} + b_{p1}x + b_{p2}x^2 + \dots + b_{pp}x^p. \\
r[u_p(x)] &= r_p \{ 1/S_{00} + T_1^2(x)/S_{11} + T_2^2(x)/S_{22} + \dots + T_p^2(x)/S_{pp} \}^{\frac{1}{2}}. \\
T_j(x) &= x^j + \beta_{j,j-1} x^{j-1} + \beta_{j,j-2} x^{j-2} + \dots + \beta_{j0}
\end{aligned}$$

§ 4. MODEL FORMS AND ILLUSTRATIVE EXAMPLE.

In carrying out polynomial fitting, it is highly desirable to employ some form of tabulation for the various quantities to be calculated. "Model Forms" have been developed for the β -system, and these will be illustrated in this section by fitting a polynomial to the observations listed in Table II.

TABLE II.

x	y	x	y
-9.0	0.40	+0.8	2.30
-7.3	0.53	+2.8	2.85
-6.4	1.09	+3.5	3.62
-5.5	0.76	+4.8	4.50
-4.4	0.80	+6.1	6.40
-3.65	1.17	+6.25	5.08
-2.2	1.16	+7.2	6.85
-1.25	1.45	+7.9	8.10

A rough graph shows that a quadratic or cubic equation would probably provide a satisfactory fit for the points. The calculations will be carried through for the cubic; in the β -system the quadratic is obtained at the same time.

The first step is to calculate the sums S_{j0} of the powers x^j at the points of observation for $j=0$ to 6. This is best done by tabulating the powers of x in columns.

The second step is to calculate the sums M_j of the products $xy(x)$ at the points of observation. Again this is best done by tabulating the products in columns. The sum of the squares of the observations Σy^2 is calculated at the same time.

To save space the detailed calculations for these two steps are omitted.

Model Form A.

$$\alpha_{jk} = -S_{jk}/S_{kk}$$

$$a_j = M_j/S_{jj}$$

S_{00}	16	S_{10} α_{10}	- 0.35 + 0.021875	S_{20} α_{20}	+478.8775 -29.929844	S_{30} α_{30}	-179.6086 +11.22554
α_{10}	+0.021875	S_{20} $\alpha_{10}S_{10}$	+478.8775 -0.0077	S_{30} $\alpha_{10}S_{20}$	-179.6086 +10.4754	S_{40} $\alpha_{10}S_{30}$	+22807.411 -3.929
$=\beta_{10}$	+0.021875	S_{11}	478.8698	S_{21} α_{21}	-169.1332 +0.3531925	S_{31} α_{31}	+22803.482 -47.61938
α_{20} $\alpha_{21}\beta_{10}$	-29.929844 +0.00773	α_{21}	+0.3531925	S_{40} $\alpha_{20}S_{20}$ $\alpha_{21}S_{21}$	+22807.411 -14332.729 -59.737	S_{50} $\alpha_{20}S_{30}$ $\alpha_{21}S_{31}$	-26553.43 + 5375.66 + 8054.02
β_{20}	-29.92211	$=\beta_{21}$	+0.3531925	S_{22}	8414.945	S_{32} α_{32}	-13123.75 + 1.559576
α_{30} $\alpha_{31}\beta_{10}$ $\alpha_{32}\beta_{20}$	+11.22554 -1.04167 -46.66580	α_{31} $\alpha_{32}\beta_{21}$	-47.61938 + 0.55083	α_{32}	+ 1.559576	S_{60} $\alpha_{30}S_{30}$ $\alpha_{31}S_{31}$ $\alpha_{32}S_{32}$	+1296991.1 -2016.2 -1085888 -20467.5
β_{30}	-36.48193	β_{31}	-47.06855	$=\beta_{32}$	+1.559576	S_{33}	188619
$M_0=M'_0$	47.06	a_0	-2.941250			Σy^2	233.7294
M_1 $\beta_{10}M_0$	+197.4100 +1.0294			M'_0a_0	138.4152	Σv_0^2	95.3142
M'_1	+198.4394	a_1	+0.4143911	M'_1a_1	82.2315	Σv_1^2	13.0827
M_2 $\beta_{20}M_0$ $\beta_{21}M_1$	+1636.283 -1408.134 +69.724			M'_2a_2	10.5441	Σv_2^2	2.5386
M'_2	+297.873	a_2	+0.0353981	M'_3a_3	1.0878	Σv_3^2	1.4508
M_3 $\beta_{30}M_0$ $\beta_{31}M_1$ $\beta_{32}M_2$	+8909.704 -1716.840 -9291.802 +2551.908			r_3	$0.674\sqrt{\left(\frac{v_3^2}{n-4}\right)}$ =0.234		
M'_3	+452.970	a_3	+0.00240151				

Model Form A (Cont.)

$$\alpha_{jk} = -S_{jk}/S_{kk}$$

$$a_j = M'_j/S_{jj}$$

a_0 = b_{00}	+2.941250						
$\beta_{10}a_1$ b_{10}	+0.009065 +2.950315	a_1 = b_{11}	+0.4143911				
$\beta_{20}a_2$ b_{20}	-1.059186 +1.891129	$\beta_{21}a_2$ b_{21}	+0.0125023 +0.4268934	a_2 = b_{22}	+0.0353981		
$\beta_{30}a_3$ b_{30}	-0.087612 +1.803517	$\beta_{31}a_3$ b_{31}	-0.113036 +0.313857	$\beta_{32}a_3$ b_{32}	+0.0037453 +0.0391434	a_3 = b_{33}	+0.00240151
$1/S_{00}$ β_{10}^2/S_{11} β_{20}^2/S_{22} β_{30}^2/S_{33}	6.25×10^{-2} 0 10.6 0.71	$1/S_{11}$ β_{21}^2/S_{22} β_{31}^2/S_{33}	0.21×10^{-2} 0 1.18	$1/S_{22}$ β_{32}^2/S_{33}	1.19×10^{-4} 0.13	$1/S_{33}$	5.30×10^{-6}
$(r_b/r_3)^2$	17.6×10^{-2}	$(r_b/r_3)^2$	1.39×10^{-2}	$(r_b/r_3)^2$	1.32×10^{-4}	$(r_b/r_3)^2$	5.30×10^{-6}
$r[b_{30}]$	9.80×10^{-2}	$r[b_{31}]$	2.76×10^{-2}	$r[b_{32}]$	2.69×10^{-3}	$r[b_{33}]$	5.38×10^{-4}

(a) Model Form A.

The sums S_{j0} of the powers x^j are entered in the first section of Model Form A and the values S_{kk} , α_{jk} ($=-S_{jk}/S_{kk}$), and β_{jk} evaluated.

The power moments M_j are entered in the second section, and the orthogonal moments M'_j and the orthogonal coefficients a_j ($=M'_j/S_{jj}$) evaluated. On the right-hand side the quantity Σy^2 is entered, the sums of the squares of the residuals Σv_p^2 determined, and the probable error r_3 of an observation of unit weight calculated for the cubic.

Next the power-series coefficients b_{pj} are calculated. The Model Form gives the coefficients of the lower degree polynomials as well as those of the cubic.

Finally, the probable errors $r[b_{3j}]$ of the cubic coefficients b_{3j} are evaluated.

The coefficients b_{3j} were checked, using the normal equations

$$\left. \begin{aligned} S_{00}b_{30} + S_{10}b_{31} + S_{20}b_{32} + S_{30}b_{33} &= M_0, \\ S_{10}b_{30} + S_{20}b_{31} + S_{30}b_{32} + S_{40}b_{33} &= M_1, \end{aligned} \right\}$$

and as a further check the residuals were found by direct calculation of the fitted values. To save space, these check calculations are omitted.

The cubic of best fit is then

$$u_3(x) = (1.804 \pm 0.098) + (0.314 \pm 0.028)x + (0.0391 \pm 0.0027)x^2 \\ + (0.00240 \pm 0.00054)x^3.$$

(b) *Model Form B.*

Suppose the fitted values $u(x)$ at the points

$$x = -20 \quad -15 \quad -10 \quad -5 \quad 0 \quad +5 \quad +10 \quad +15 \quad +20,$$

and the probable errors of these values, are required.

The quantities $T_j(x)$ at the required points are first calculated as in the upper section of Model Form B. These values are then used in the middle section to calculate the probable errors $r[u(x)]$. Finally the fitted values are calculated in the lower section.

All probable error calculations are carried out to slide-rule accuracy only.

Model Form B.

β	·0219			·353	−29·9			1·56	−47·1	−36·5	
x	β_{10}	$T_1(x)$	x^2	$\beta_{21}x$	β_{20}	$T_2(x)$	x^3	$\beta_{32}x^2$	$\beta_{31}x$	β_{30}	$T_3(x)$
−20	·0219	−20	400	−7	−29·9	363	−8000	624	+942	−36	−6480
−15		−15	225	−5		190	−3375	351	+706		−2360
−10		−10	100	−4		66	−1000	156	+471		−409
−5		−5	25	−1·8		−6·7	−125	39	+235		+113
0		0	0	0		−30	0	0	0		−36
+5		+5	25	+1·8		−3·1	+125	39	−235		−107
+10		+10	100	+4		74	+1000	156	−471		+649
+15		+15	225	+5		200	+3375	351	−706		+2980
+20		+20	400	+7		377	+8000	624	−942		+7640

S_{jj}	16	479	8410	189×10^3	r	0·234
x	$1/S_{00}$	T_1^2/S_{11}	T_2^2/S_{22}	T_3^2/S_{33}	$(r[u(x)]/r)^2$	$r[u(x)]$
−20	0·0625	0·84	15·6	222	238	3·6
−15		0·47	4·3	29·4	34·3	1·37
−10		0·208	0·518	0·89	1·68	0·30
−5		0·052	0·005	0·068	0·187	0·101
0		0	0·106	0·007	0·175	0·098
+5		0·052	0·001	0·061	0·177	0·098
+10		0·208	0·65	2·22	3·16	0·42
+15		0·47	4·7	47·2	52·4	1·70
+20		0·84	16·9	309	327	4·2

x	b_0	b_1x	b_2x^2	b_3x^3	$u_3(x)$
−20	1·804	6·278	15·64	19·2	−8·0 ±3·6
−15		4·709	8·80	8·10	−2·2 ±1·4
−10		3·139	3·91	2·40	+0·17 ±0·30
−5		1·570	0·978	0·300	+0·91 ±0·10
0		0	0	0	+1·80 ±0·10
+5					+4·65 ±0·10
+10					+11·25 ±0·42
+15					+23·4 ±1·7
+20					+42·9 ±4·2

§ 5. DISCUSSION OF ILLUSTRATIVE EXAMPLE.

(a) *Arithmetical Calculations.*

The calculations in §4 were carried out on a hand-operated Brunsviga calculating machine. Seven-figure accuracy in multiplication and division was obtainable without trouble.

It will be observed that there is a loss of one significant figure in the calculations of S_{33} , a_2 , a_3 . In the present example the loss in accuracy is unimportant. If the scatter of the observations is small, it may be necessary to obtain the coefficients to a greater accuracy. This may be done by calculating more significant figures for the earlier quantities in Model Form A, particularly α_{10} , α_{20} , β_{20} and S_{11} . These can be calculated accurately without trouble, since the number of figures in S_{00} , S_{10} , S_{20} is usually small.

If the scatter of the residuals is small, it is desirable that the terms in the calculation of Σv^2 should be accurate to the same number of figures as Σy^2 . It may be an advantage to use the alternative forms M_0^2/S_{00} , M_1^2/S_{11} , etc. for these terms. If it is not possible to calculate the terms with sufficient accuracy, the individual residuals will have to be calculated.

Unless the person doing the fitting is an experienced computer, it is almost essential that each calculation should be checked before proceeding with the next. Whenever possible the check should be done in a different way. If desired, a check column can be introduced in the calculations of the quantities S , α , as in the Doolittle scheme. However, the check column does not provide a safeguard against small errors, since one or more of the values which go to make up the check column entry usually are considerably larger than the others.

In the fitting of curves of higher degree than the third, the arithmetic becomes extremely tiresome. Fortunately, in many applications, a quadratic or cubic provides a satisfactory fit. If it is necessary to fit a higher degree polynomial, the Model Forms may be extended to include the extra terms.

(b) *Choice of the Degree of the Polynomial.*

Birge (1947) has proposed a criterion using the values Σv^2 (as in Model Form A) for deciding on the degree of the most suitable polynomial. Increasing the degree from $j-1$ to j at first reduces Σv^2 by a large factor. Soon a value p is reached, such that for values of j greater than p the reduction in Σv^2 is small. The polynomial of degree p then provides the best fit for the observations.

In the illustrative example it would appear that the quadratic would give almost as good a fit as the cubic. However, if the individual residuals are examined, it will be found that the two observations at $x=6.1$ and $x=6.25$ contribute 1.10 to the value 1.45 of Σv^2 . For the quadratic the contributions from these observations amount to 1.09 in a total of 2.54. In fact, any least squares polynomial of reasonable

degree must pass more or less centrally between these points. It would be legitimate to subtract the contributions from these observations before comparing the values Σv^2 . The contributions from the remaining observations amount to 1.45 and 0.35 for the quadratic and cubic respectively.

The cubic should then provide an appreciably better fit. Comparison of the graphs of the quadratic (dotted line) and cubic (solid line) in fig. 1 shows that this is indeed so.

Fig. 1.

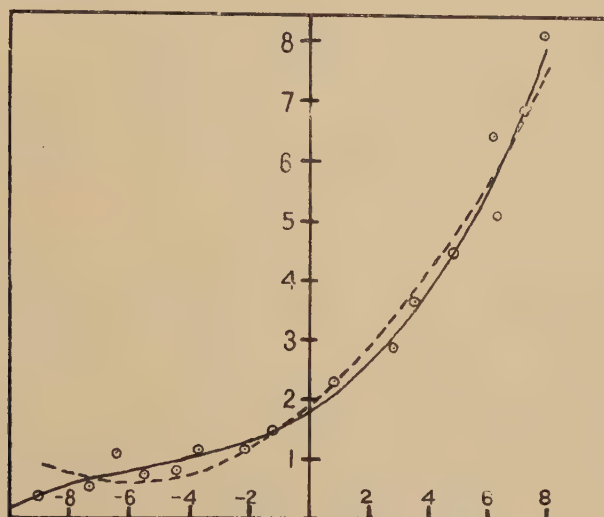


Fig. 1

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XI. *Emission of Protons and Alpha-Particles in High Energy Cosmic Ray Stars.*

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1. SUMMARY.

This paper describes measurements of the energy, angular and frequency distributions of protons and alpha-particles in disintegrations of the silver and bromine nuclei of nuclear emulsions, at excitation energies comparable with and larger than the binding energy (~ 700 MeV.).

Only those charged particles with ionization greater than six times minimum have been considered (*i.e.* greater than that of a 50 MeV. proton). The star disintegrations were observed in Ilford C2 plates, $100\ \mu$ thick, exposed at Jungfraujoch (3457 m.).

2. RATIO OF NUMBERS OF ALPHA-PARTICLES TO PROTONS FROM STARS.

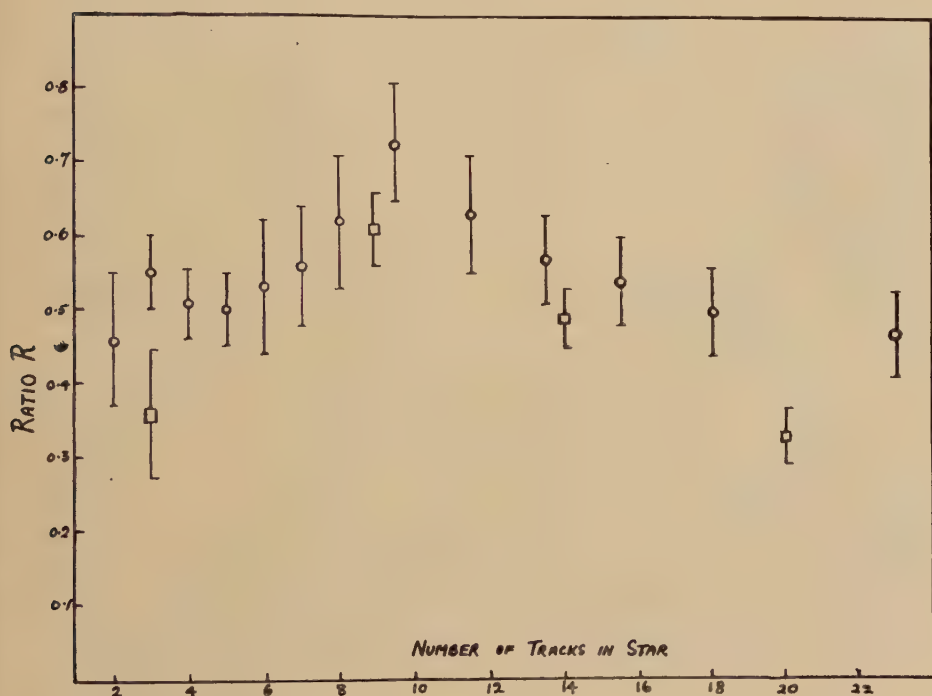
A QUANTITY of interest in the theory of nuclear disintegrations is the ratio (α/p) of the numbers of alpha-particles to protons emitted at different excitation energies. Fig. 1 shows the result of measuring, for different prong number N , the ratio R of numbers of particles, charge ≥ 2 , to singly charged particles. It has already been shown (Harding, Lattimore and Perkins 1949) that the great majority of the singly charged particles (~ 85 per cent) consist of protons. In order to obtain the true α/p ratio in AgBr nuclei, however, two main corrections to R are required. For $N < 6$, the α/p ratio in AgBr is less than R , because of the contribution of the light gelatine atoms in the emulsion (Perkins 1949 a). The latter have an α/p ratio of about unity. From the known proportion of stars of $N < 6$ due to carbon, oxygen and nitrogen (Harding 1949 a), we thus obtain $(\alpha/p)_{\text{AgBr}}$ for $N=3$ as indicated in the graph. Secondly, especially for high values of N , particles heavier than alpha-particles are frequently emitted from stars (Perkins 1949 b). The result of subtracting these from R is indicated for stars of 7–11 prongs ($\bar{N}=9$), 12–16 prongs ($\bar{N}=14$) and 17–31 prongs ($\bar{N}=20$). From the four true values of $(\alpha/p)_{\text{AgBr}}$ thus obtained, it is clear that the α/p ratio is not a monotonic function of excitation energy. The initial increase is easily understandable, since as the temperature, and therefore kinetic energy of the emitted particles increases, the relative height of the potential barrier to alpha-particles and protons becomes less important. As N increases further, α/p appears to reach a broad maximum in the region $N=10$. A maximum in the

* Communicated by Sir George Thomson.

† Now at H. H. Wills Physical Laboratory, University of Bristol,

ratio at just this excitation energy (~ 300 MeV) has been predicted by Le Couteur (1949) on the evaporation model. It is to be expected that the emission probability for alpha-particles will decrease when the nuclear temperature exceeds half the binding energy of a nucleon in an alpha-particle.

Fig. 1.



Ratio, R , of number of particles of charge greater than 2, to singly charged particles, for stars, of different prong number. $\square$ Corrected values of R , giving true alpha/proton emission ratio. Vertical lines indicate standard deviation.

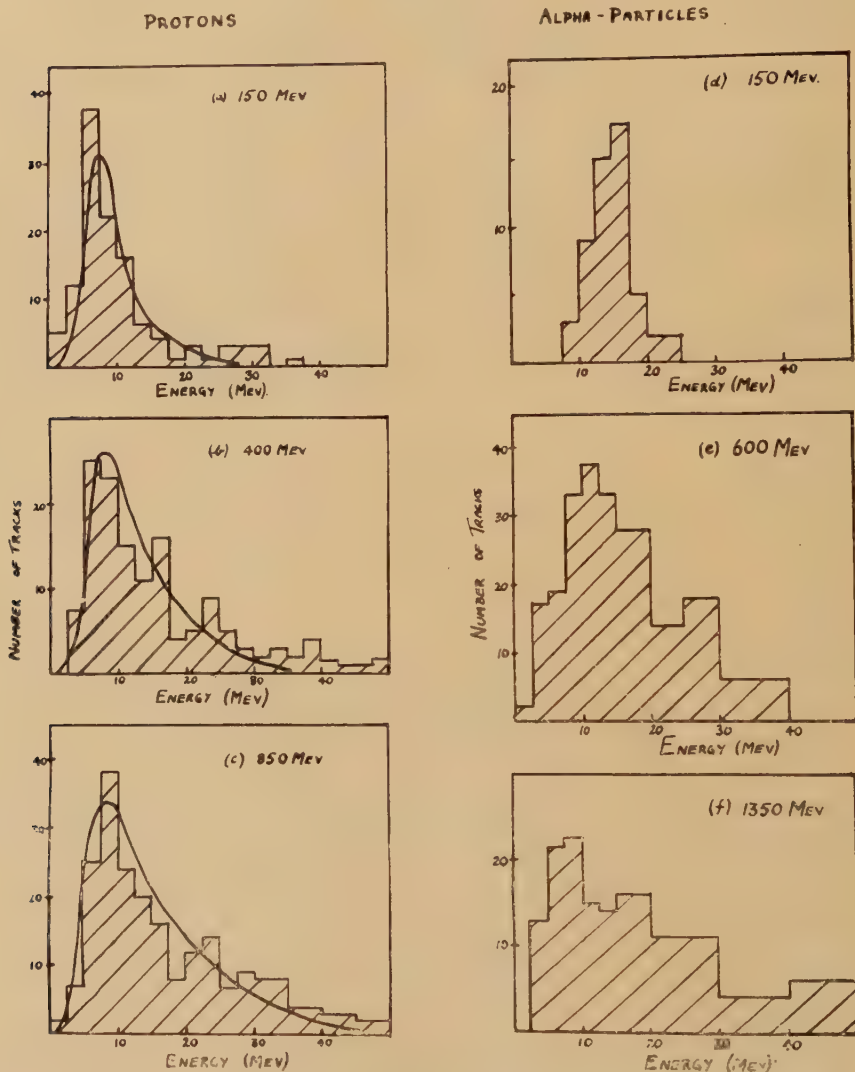
3. ENERGY DISTRIBUTION OF SINGLY AND DOUBLY CHARGED PARTICLES.

(i) Protons.

The method of obtaining the energy distributions of the singly charged particles, predominantly protons, and alpha-particles has already been described (Harding, Lattimore and Perkins 1949). It was shown in this paper, hereafter referred to as HLP, that the energy distribution of the protons was consistent with the evaporation model of the nucleus. This model assumes that the energy transferred to the nucleus by the incident particle is distributed statistically among the nucleons, by successive collisions, before disintegration proceeds; thus any one nucleon has to undergo several collisions before it may acquire sufficient energy to escape

from the nucleus (we exclude of course those nucleons "knocked on" directly by the star-producing particle, and contributing a high-energy "tail" to the Maxwellian distribution).

Fig. 2.



Energy distribution of protons and alpha-particles emitted from silver and bromine nuclei at different excitation energies. Protons: (a) 150 MeV.; (b) 400 MeV.; (c) 850 MeV. Full curves show the calculated evaporation distributions. Alpha-particles: (d) 150 MeV.; (e) 600 MeV.; (f) 1350 MeV.

The proton energy distributions, as given in HLP, are reproduced in fig. 2 (abc). Each histogram is taken from a group of stars with the mean excitation energies indicated. The latter were calculated by assuming the emission of that number of neutrons which would result in a stable residual nucleus. The curves were calculated assuming the

free-particle model, with corrections. We see that the thermodynamical picture of the disintegration holds good for emission of protons (and presumably neutrons), even at excitation energies larger than the total nuclear binding energy (~ 700 MeV.). A more detailed analysis, also based on the Fermi-gas model, has recently been given by Le Couteur (1949) and by Fujimoto*.

(ii) *Alpha-particles.*

The energy distributions of the alpha-particles are also given in fig. 2 (*def*). In the distribution at 150 MeV. excitation energy (fig. 2*d*) which corresponds to stars of small prong number, the contribution from the light emulsion nuclei has been subtracted by a method previously described (Perkins 1949a). Fig. 2*d*, together with evidence described below, shows that the emission of alpha-particles in small stars may be treated as an evaporation process, most of the alpha-particles having energies greater than the barrier potential (10–12 MeV.). As the excitation energy increases, the distributions extend to higher energies, as do those of the protons, but we also obtain an increasing proportion of low-energy alpha-particles. In fact, the most probable energy of the alpha-particles *decreases* as the excitation energy increases. The reduction in effective barrier may perhaps be explained by a mean increase in nuclear radius due to surface oscillations, as suggested by Bagge (1943). Even so, it is not possible to understand why, if all the alpha-particles are released in a process of evaporation, there is a reduction in barrier for them but not for the protons. We must conclude that a considerable fraction, at least, of the alpha-particles are released in a different process. This will almost certainly be a preliminary process, when the nucleus is very "hot", the reduction in barrier large, and thermal equilibrium not yet attained.

4. ZENITH-ANGLE DISTRIBUTION OF PROTONS AND ALPHA-PARTICLES.

A second difference in behaviour between protons and alpha-particles is revealed in their angular distributions with respect to the vertical.

If the stars are produced by primaries travelling downwards—in what follows we assume they are travelling vertically downwards—then the emitted particles should have a downward component of momentum. Let us assume that the alpha-particles, protons and neutrons leave the nucleus in an evaporation process, that is, the parent nucleus has taken up the whole momentum transfer from the primary before it disintegrates. Since, in producing a large star, the primary is likely to make several collisions in traversing the nucleus, the sideways components of momentum transfer tend to cancel out (alternatively, if there is only one very violent collision, several mesons may be produced and re-absorbed; all will be strongly directed downwards. This is equivalent to several collisions by the primary). We assume therefore that the net momentum transfer is vertically downwards, and furthermore that it is numerically equal

* Y. Fujimoto, private communication.

to the energy transfer (*i. e.* the star is produced by a relativistic primary which also has relativistic energy after leaving the nucleus). All these assumptions seem reasonably well borne out by the observations of Harding (1949 b) on the smaller stars, and we want to investigate their validity in the larger ones.

Let u be the downward velocity of the nucleus as a result of the impact, $\bar{v}$ the average observed velocity of emission of an evaporating particle. We define $\bar{v} = \sqrt{(2\bar{E}/M)}$, where $\bar{E}$ is the average energy of a particle, M the mass. If $u \ll \bar{v}$, as is indeed always the case, it can be shown that, assuming a Maxwellian energy distribution (HLP), the downward excess of particles should constitute a fraction $\sqrt{(\pi/2)} \cdot u/\bar{v}$ of the total, since the angular distribution of the particles in the coordinate system of the nucleus will be isotropic. u , as calculated from the mass of the nucleus and the energy transfer, can therefore be compared with the u obtained from the observed fractional downward excess of particles.

In the accompanying table, it can be seen that, if we take protons, neutrons and alpha-particles together, there is reasonably good agreement between the calculated and observed values of u (we assume the fractional downward excess of the neutrons, and their mean emission velocity, equal to that of the protons). In the group of smaller stars (7-11 prongs), with excitation energies well below the total binding energy, the ratio of downward velocities u_α/u_p , of alpha-particles to protons does not differ significantly from unity, in agreement with the hypothesis of evaporation. At higher energies, however, the downward excess of alpha-particles becomes extremely small and that of the protons correspondingly larger.

TABLE I.

Number of tracks in star	17-31	12-16	7-11
Estimated excitation energy (MeV.) = momentum transfer (MeV./c)	1350	750	420
Downward velocity of nucleus = u/c	0.013	0.008	0.0045
Fractional downward excess of—			
protons	(98 ± 24)/600	(53 ± 23)/513	(21 ± 16)/279
alpha-particles	(6 ± 18)/322	(12 ± 17)/296	(18 ± 13)/168
Average downward velocity of—			
(alphas + protons + neutrons) ..	0.013 ± 0.004	0.008 ± 0.004	0.007 ± 0.004
protons u_p/c	0.025 ± 0.006	0.014 ± 0.006	0.009 ± 0.007
alphas u_α/c	0.002 ± 0.006	0.003 ± 0.004	0.006 ± 0.004
Ratio of downward velocities u_α/u_p	0.08 ± 0.24	0.21 ± 0.28	0.68 ± 0.74

It is not of course possible to say if the process responsible for this behaviour, which appears to set in at excitation energies above 400 MeV., is also that which produces the reduction in effective barrier described above. A possible explanation, put forward by HLP, is as follows. Assume that, in a preliminary process, there is a "boiling off" of alpha-particles following intense localized "heating" in the top of the nucleus. Those travelling upwards escape clean away from the nucleus, whilst those travelling downwards are stopped by collisions and lead to a general

warming up of the entire nucleus, succeeded by evaporation. The downward excess of alpha-particles which subsequently evaporate together with the protons may thus be cancelled out, and the whole nucleus will receive an additional downward momentum from the alphas travelling upwards in the preliminary process, thus accounting, in some degree at least, for the large downward excess of protons. Poor statistics do not allow us to investigate such processes in detail.

A second hypothesis, which is supported by experimental evidence, is that heavy fragments are emitted at high excitation energies, and that these are usually unstable and disintegrate spontaneously into alpha-particles. The latter then have to overcome a potential barrier much lower than that of the parent nucleus. Experimental evidence on the distribution of such fragments (Perkins 1949 b) is at present not sufficient to throw light on any resulting anomaly in the zenith-angle distribution of the alpha-particles.

It is to be pointed out that the observations above were made on those protons of energies below 50 MeV. However, these would include a few not produced in the evaporation process, but knocked-on directly by the primary particle. Suppose these knock-ons constitute a fraction f of all the protons. Since they should all travel downwards, they contribute approximately an additional fractional downward excess f , if $f \ll 1$. f is difficult to estimate, but it can be seen from the histograms of fig. 1 that it is not likely to exceed 0.1 in the large stars (*i. e.* less than half the total observed excess for protons). This can to a large extent account for the increased downward excess in such stars.

It can be concluded that both the energy and zenith-angle distributions of protons, and presumably neutrons, can be explained very satisfactorily on the evaporation picture, even at excitation energies considerably in excess of the total nuclear binding energy; but that the corresponding distributions for alpha-particles, in stars involving more than 400 MeV. energy, are inconsistent with such a picture. The elucidation of the mechanism of alpha-particle emission awaits further experimental evidence.

ACKNOWLEDGMENTS.

I should like to express my thanks to Dr. E. P. George and his staff, of Birkbeck College, London. About a third of all the stars represented in the above analysis were taken from plates kindly loaned by Dr. George; and without his generous cooperation these measurements would not have been possible.

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*XII. On the Fine Structure near the FeK-absorption Edges in the
Various Oxides of Fe.*

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[Received November 1, 1949.]

SUMMARY.

After a review of the theoretical interpretation of the fine structure in X-ray absorption edges, new measurements on the K-edges of different compounds of iron at low dispersion are described. From these in conjunction with our earlier measurements at high dispersion (Coster and Kiestra 1948)† the following conclusions may be drawn with respect to these compounds.

(a). In a region up to about 70 eV. from the edge the behaviour of the absorption coefficient is mainly a property of the atom in question.

(b). In a region between 70 and 175 eV. the fine structure is determined by the immediate surroundings of the atom.

(c). In the region above 175 eV. the fine structure depends essentially on the crystal lattice.

This is in accordance with the notion that as the energy of the ejected electron increases it penetrates further into the lattice.

§ 1. THEORETICAL FOUNDATIONS.

IF the absorption coefficient of X-rays is considered in its dependence upon the frequency of the radiation, it may in general be stated that the absorption decreases with increasing frequency. Every time, however, that a critical frequency is surpassed, the absorption suddenly increases. This is caused by the fact that at these frequencies a new possibility of absorption arises, accompanying the removal of, for instance, a K- or L-electron from the atom. The corresponding phenomenon is called the K- or L-edge. On the short wavelength side of these edges the variation in the absorption is not monotonic, but fluctuates over a distance of several hundred volts. The difference between successive maxima and minima of the absorption coefficient may easily amount to 10–20 per cent. Of this phenomenon, which is called the fine structure of X-ray absorption edges, a theory based on wave mechanics was given by Kronig (I., 1931; II., 1932) for the case where the absorbing element forms part of a crystalline solid. According to this theory the material waves, representing an electron which by absorption of an X-ray quantum is removed from an inner shell of an atom and traverses the crystal lattice

* Communicated by the Authors.

† In the following part we will indicate this article as I.

in a certain direction with a certain energy, suffer diffraction at the crystal lattice. The Bragg reflections, occurring at certain wavelengths and preventing the electron from entering the crystal (forbidden energy zones), even when averaged over all directions of ejection, still leave a fluctuation in the absorption probability as function of the wavelength of the electron or of the corresponding X-ray frequency.

Already in his first paper Kronig was able to show that several peculiarities of the fine structure of X-ray absorption edges could be explained on the basis of his theory. It is for instance evident that metals, crystallizing in the same lattice type, should have the same type of fine structure. It could indeed be shown experimentally (Coster and Veldkamp 1932) that for ejected electrons of the same sort (s- or p- etc. electrons) and for atomic numbers not too far apart this was the case. Furthermore, the distances of the maxima and minima of absorption from a suitable zero point corresponding to the average potential in the crystal appeared to be inversely proportional to the square of the lattice constant, as was predicted by the theory. If the crystal structure is changed by using an alloy instead of the pure element, the fine structure changes in the expected way (Coster and Klammer 1934, I.), the same being true in those cases where the crystal type is altered by heating (Coster and Levi 1939).

The fine structure of X-ray absorption edges is also observed when the absorbing element forms part of a polyatomic molecule (Coster and Klammer 1934, II.). For this case too a theory was given by Kronig (1932 III.). By absorption of an X-ray quantum an electron of an inner shell is removed with an excess of energy from the atom. The corresponding material waves are scattered by the other atoms of the molecule, and the resultant wave built up from the primary and the scattered waves determines the probability of absorption of the different X-ray frequencies. At first sight this method of calculation of fine structure might seem in principle to be different from that used in the case of crystalline solids; on closer inspection, however, it is clear that also in the last case, instead of regarding the Bragg reflection of the material waves at the crystallographic planes, we may equally well determine the resultant wave built up by the primary wave and the secondary ones scattered by the surrounding atoms. In this process the atoms at short distance play a larger part than those farther removed. Coster (1935) was able to show that metals crystallizing in a cubic close-packed lattice have the same type of fine structure as those crystallizing in a hexagonal close-packed lattice, as long as attention is paid only to the relative *positions* of the successive maxima and minima of absorption, while some differences are noted when also their *form* is taken into account. This was associated with the fact that in both types of crystal lattices the immediate surroundings of an atom are formed by the same number of atoms, whereas differences in the arrangement of surrounding atoms are only observable for larger distances.

Kronig's theory treats the electron liberated from the atom as almost free, so that the forces exercised by the lattice may be regarded as small perturbations. This implies that the rules stated above are valid only at some distance from the zero potential. In the case of metal crystals this distance appeared to be more than 70 volts from the edge. Moreover, on the experimental side, the fine structure, as it is usually observed, arises by the absorption of non-polarized X-rays in a polycrystalline substance and consequently the fluctuations in the absorption coefficient which still remain represent an effect, averaged over all directions of ejection in the crystal. We thus understand that the fine structure of absorption edges is a rather rough phenomenon, and it may be regarded as a fortunate circumstance that in verifying experimentally the above-mentioned rules use was made in the present laboratory of X-ray spectrographs with not very high dispersion. Indeed, it is not difficult to ascertain that by using too large a dispersion we should easily run the risk of overlooking the general features mentioned.

If, however, it is desired to study the phenomena arising within a short distance from the main edge, the dispersion formerly used in this laboratory is no longer sufficient. A larger dispersion may be obtained firstly by the bent crystal method used by Cauchois (1948) and co-workers and Sanner (1941). Some American investigators (Barnes 1933, Beeman and Friedman 1939, Bearden and Snyder 1941), using the double crystal spectrometer, got very interesting results not obtainable with a smaller dispersion. They investigated a region within about 50 volts from the main edge, about which Kronig's theory does not give any information. Indeed, to explain the fine structure of X-ray absorption edges, in general, one has to bear in mind that in the corresponding transition an electron from an inner shell is removed to one of the unoccupied levels in the lattice. To calculate the corresponding absorption it is necessary to determine the density of states of these unoccupied levels. This can be done in two different ways:—

(1e) By starting from the wave function of a free electron.

(2e) By starting in zero approximation from the wave function of a free atom.

As has already been stated, the first procedure has been employed by Kronig, who calculated the perturbation caused by a periodic potential that serves to approximate the lattice field. It can only be applied if the energy of the electron in the lattice is large compared with the variations in the potential.

The second method has been developed by Wigner and Seitz (1933) and Slater (1934). It has been applied by Krutter (1935) to calculate the band structure in the case of Cu for the occupied levels with highest energy and the unoccupied levels to a distance of 20 volts from the Fermi-limit.

The K-absorption edge of Cu, taken by Beeman and Friedman (1939) is in good agreement with the theory of Krutter. The agreement is even better than could be anticipated from the approximations used.

In recent times it has been shown that by using the photographic method with the single crystal tube spectrograph the same dispersion and the same resolving power may be obtained as with the double crystal spectrometer (Coster and de Lang 1947). As the dispersion and resolving power of the spectrograph in question depend upon its dimensions, it is necessary to enlarge these. By constructing a spectrograph with a radius about five times as large as that formerly used in this laboratory, we (Coster and Kiestra 1948) were actually able to obtain results comparable in quality to those of the American authors just mentioned. At the same time, by applying some new devices we succeeded in compensating for the loss of energy caused by the increased dimensions.

While hitherto attention has been directed principally to metals, especially those of the transition periods, it seemed important to carry out an analogous investigation for compounds. There the situation is more involved due to the presence of several kinds of atoms, the greater complication of the lattice structure and the fact that a given sort of atom may have different valencies and even different surroundings in the same lattice. Measurements at high dispersion have already been published by Yoshida (1941, compounds of Fe, dispersion not very great), Sanner (1941, compounds of many transition metals), Beeman and Bearden (1942, aqueous solution of salts of Ni, Cu and Zn), Coster and Kiestra (1948, oxides of Fe and Mn) and Hanson and Beeman (1949, compounds of Mn).

In order to bring out also in the case of compounds the typical difference in the behaviour of the fine structure close to and far from the edge, we present in this publication results on the oxides of Fe taken at low dispersion with the purpose of comparing them with our earlier measurements on the same compounds at high dispersion.

§2. EXPERIMENTAL METHOD.

For these experiments the same spectrograph was used as for the investigations at high dispersion in I. The tube between the X-ray tube and the crystal and the tube containing the photographic plate holder were replaced by others, the distance focus-crystal and also crystal-photographic plate being reduced from 115 to 32.5 cm. in each case. In this way the dispersion decreased in the ratio 3.5 while the region investigated increased in the same ratio, *i. e.* to 400 eV. from the absorption edge.

Instead of tungsten molybdenum was now used as target to avoid the tungsten L η emission line at 1675 X.U. Besides the tungsten hot wire was replaced by an oxide-coated platinum cathode. Care was taken that the NiK α_{12} lines were absent as much as possible so that also the fine structure in the region of 1660 X.U. could be determined.

The analysing crystal was a calcite crystal that remained fixed during the exposures. In the beginning the crystal had been carefully ground, polished and etched. A time of about 20 hours was then necessary for one exposure. As the resolving power of the spectrograph is relatively small at these dimensions, it became evident that the crystal does not need to have a high resolving power either. Therefore during the last exposures a crystal was used that had been ground, polished, but not etched, giving the same results in about five hours. This reduction in the time of exposure was very favourable, the intensity of the scattered radiation being diminished by a factor 4, compared with the former exposures.

Agfa Blau Hart plates were used. These are not as sensitive as Ilford Zenith plates but they have a finer grain. On the other hand always at least two exposures of the same substance were made and only those peculiarities were taken for granted which were present on two (or more than two) plates.

From the photographic plates photometer curves were taken with a Moll-photometer, using a beam of light of a height of 3 cm., which is the height of the photographed spectrum. In this way the grains of the plates do not spoil the curves very much.

In I. all the photometer curves were changed into intensity curves with the aid of a blackening scale for each plate. As can be seen from the figs. 5 and 6 in I. on the one hand and figs. 7 and 8 on the other, the main form of the curves as a whole is practically the same. For that reason in the present article only the photometer curves are given. The most interesting feature of these curves is the position and form of the maxima and minima of absorption.

§3. RESULTS.

In order to bring out the influence of the dispersion on the aspect of the fine structure we reproduce in figs. 1 and 2 the results for the K-edge found for Fe and published already elsewhere*. Furthermore, we show in figs. 3 and 4 the analogous photometer curves as found for various oxides of Fe, while fig. 5 gives a comparison at low dispersion of FeF_2 , Fe_3O_4 and FeS .

As appears from figs. 1 and 2, the diminution in the dispersion causes a reduction in resolving power. In fact the minima α and β in fig. 1 are no longer separated in fig. 2. In addition the structure in the edge has become entirely invisible.

Fig. 1, embracing only a region of about 70 volts, is identical with the curve obtained for metallic iron by Beeman and Friedman (1939) with

* We call attention to the fact that just as in I. we deviate from the usage in the earlier literature by taking increasing absorption in the upward direction and increasing energy to the right. In addition for Fe the designation of the maxima differs from that of Coster and Veldkamp, an additional maximum having been discovered at the higher dispersion.

the double crystal spectrometer and entirely of the same type as the curves obtained for metallic manganese by Coster and Kiestra (1948) and by Hanson and Beeman (1949). An interpretation of this curve with which we can fully agree, has been given for the first time by Beeman and Friedman on the basis of the theoretical considerations of Krutter (1935) for Cu, already mentioned in the introduction.

Fig. 2, on the other hand, at a distance of more than 70 volts from the main edge to a distance of about 400 volts, shows the typical fine structure of the body-centred cubic lattice of which the form is in excellent agreement with the theory of Kronig. How strongly this fine structure is characteristic for this crystal type has moreover been shown by Coster and Veldkamp (1932) and Coster and Klammer (1934, I.).

Fig. 1.

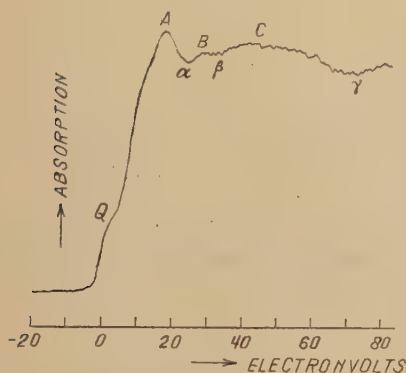
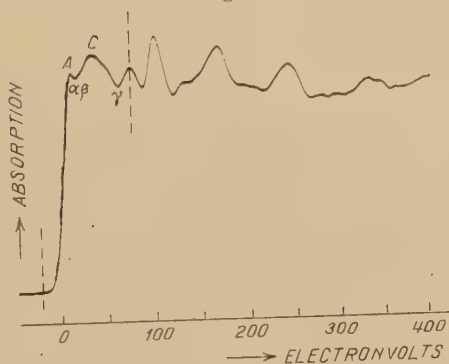


Fig. 2.



Photometer curve at $\frac{1}{2}$ natural size of Fe K-absorption edge of metallic iron at high dispersion.

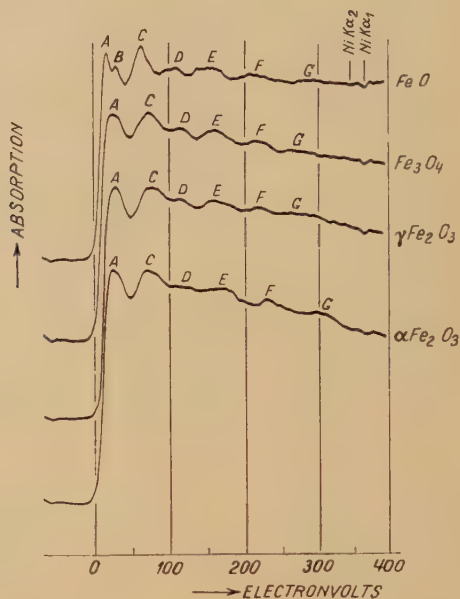
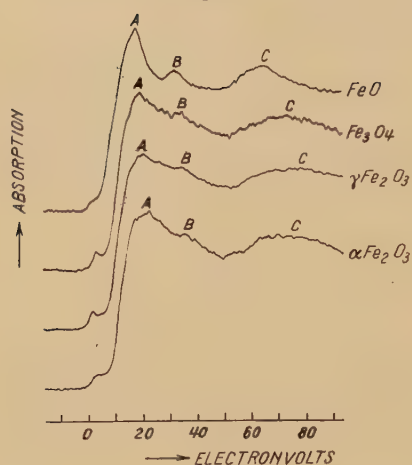
Photometer curve at $\frac{1}{2}$ natural size of Fe K-absorption edge of metallic iron at low dispersion. The region corresponding to the whole of fig. 1 is denoted by dotted lines.

Comparison of figs. 3 and 4 shows that here, too, at low dispersion the maxima α and β are only separated for FeO. The initial absorption, clearly apparent at high dispersion as a small maximum to the left of the main edge, is practically unresolved at low dispersion.

The most striking feature of fig. 4 is that the form of the fine structure in the region between 70 and 175 eV. is almost identical for all the oxides: two minima with one maximum (D) in between. Fig. 5 shows on the other hand that for FeS and FeF₂ in this region the structure is quite different. From this we conclude that the fine structure here is mainly due to the O-ions surrounding the Fe-ion. An additional argument is that the extrema for the ferrous ion, which is larger, lie closer to the edge than those for the smaller ferric ion. The fine structure in this case may be compared with that of polyatomic molecules in gases. The result is also reminiscent of that obtained by Coster (1935) in the case of cubic face-centered and hexagonal lattices already mentioned in § 1.

Fig. 4.

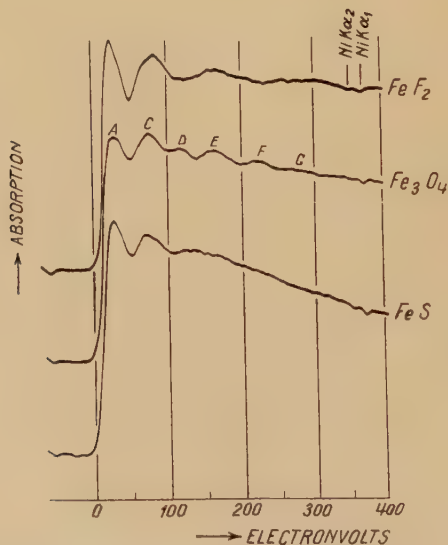
Fig. 3.



Photometer curves at $\frac{2}{5}$ natural size of Fe K-absorption edges of the iron oxides at high dispersion.

Photometer curves at $\frac{2}{5}$ natural size of Fe K-absorption edges of the iron oxides at low dispersion.

Fig. 5.



Photometer curves at $\frac{2}{5}$ natural size of Fe K-absorption edges of three iron compounds at low dispersion.

Regarding the fine structure for the oxides above 175 eV. we see that the extrema lie in different places for α Fe_2O_3 and γ Fe_2O_3 , while γ Fe_2O_3 and Fe_3O_4 behave in an identical way. Now it is known that the α - and γ -modifications have different crystal structures, while γ Fe_2O_3 and Fe_3O_4 both are spinels with almost the same lattice constant. From this one concludes that the fine structure above 175 eV. is principally determined by the lattice type of these compounds. For crystals of metals the same is true above 70 eV.

Summarizing, we may say that as the energy of the ejected electron is increased the region of the crystal that plays a rôle in determining the fine structure is extended more and more.

The writers are greatly indebted to Professor R. Kronig for his advice in the completion of this report.

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XIII. Gravitational Fields of Spherical Symmetry and Weyl's Conformal Curvature Tensor.

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ABSTRACT.

Solutions of the gravitational field equations of relativity are considered, so that the metric is non-static and has spherical symmetry, satisfying at the same time the additional equations, $C^{h}_{ijk, h}=0$, where the tensor C^{h}_{ijk} is Weyl's conformal curvature tensor. The additional equations always hold good, whatever be the metric, when $R_{ij}=0$, but when $R_{ij}\neq 0$ it is shown that the only spherically symmetrical solution of physical significance is what is known as Schwarzschild's internal solution. For the most general gravitational metric of spherical symmetry considered here, the condition $C^{h}_{ijk}=0$ reduces to one equation only, which is one of those following from $C^{h}_{ijk, h}=0$; and thus the corresponding space-time is conformal to flat space-time even when the latter condition alone is satisfied.

1. INTRODUCTION.

A GRAVITATIONAL field is distinguished from flat space-time by the conditions,

$$\left. \begin{array}{l} \text{(i.) } R_{hijk}=0, \text{ for flat space-time,} \\ \text{(ii.) } R_{hijk}\neq 0, \text{ for a gravitational field,} \end{array} \right\}, \quad \dots \quad (1)$$

where R_{hijk} is the Riemann-Chrystoffel curvature tensor. When (ii.) is satisfied the distribution of matter and motion follows from the contracted tensor R_{ij} . Weyl's conformal curvature tensor C^{h}_{ijk} connects the contracted and original tensors by the equation (Eisenhart 1926) :

$$C^{h}_{ijk}=R_{hijk}+\frac{1}{2}(g_{jh}R_{ik}-g_{hk}R_{ij}+g_{ik}R_{jh}-g_{ij}R_{hk})+\frac{R}{6}(g_{hk}g_{ij}-g_{hj}g_{ik}). \quad \dots \quad (2)$$

It is well-known that

$$C^{h}_{ijk}=0, \quad \dots \quad (3)$$

is a necessary and sufficient condition for the space-time to be conformal to flat space-time. It can be immediately verified that the contracted tensor, C_{ij} , vanishes identically :

$$g^{hk}C^{h}_{ijk}\equiv C_{ij}=0. \quad \dots \quad (4)$$

* Communicated by the Authors.

Thus the very structures of the three tensors give ten independent components for C_{hijk} , ten for R_{ij} and 20 for R_{hijk} . Moreover, the Bianchi identity, viz.,

$$R^h_{ijk,l} + R^h_{ikl,j} + R^h_{ilj,k} = 0, \quad . \quad . \quad . \quad . \quad . \quad (5)$$

leads to

$$C^h_{ij,h} = \frac{1}{2} R_{ij}, \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where (Eisenhart 1926)

$$R_{ij} = R_{il,j} - R_{ij,l} + \frac{1}{6} (g_{ij} R_{,l} - g_{il} R_{,j}), \quad . \quad . \quad . \quad . \quad (7)$$

in the usual notation. It is clear from (6) that in the unoccupied portions of a gravitational field where

$$R_{ij} = 0, \quad . \quad . \quad . \quad . \quad . \quad (8)$$

we have also

$$C^h_{ij,h} = 0. \quad . \quad . \quad . \quad . \quad . \quad (9)$$

(9) is also true when the space-time is conformal to flat space-time, that is, when (3) holds good, whatever may be the distribution of matter and motion.

Apart from the considerations outlined here little is known of the gravitational significance of the tensor C_{hijk} . The following is an attempt to investigate it further in relation to distributions of spherical symmetry for which the most general metric may be taken as

$$ds^2 = -e^{\lambda} dr^2 - r^2 (d\theta^2 + \sin^2 \theta d\phi^2) + e^{\nu} dt^2, \quad . \quad . \quad . \quad (10)$$

where $\lambda = \lambda(r, t)$, $\nu = \nu(r, t)$. While (3) implies (9) in the general case it is found that, for (10), the latter implies the former.

2. THE CONDITION, $C_{hijk} = 0$.

For the metric (10) the components of R_{ij} which are not identically zero are

$$R_{11}, R_{22}, R_{33}, R_{44}, R_{14}, R_{41}$$

with

$$R_{33} = R_{22} \sin^2 \theta, \quad R_{14} = R_{41}. \quad . \quad . \quad . \quad . \quad (11)$$

They condition (3) implies ten equations, many of which are identically satisfied, the rest giving only one independent equation, viz.,

$$(1 - e^{-\lambda}) + \frac{1}{2} r e^{-\lambda} (\nu' - \lambda')^2 + r^2 e^{-\nu} \left(\frac{1}{2} \ddot{\lambda} - \frac{1}{4} \dot{\lambda} \dot{\nu} + \frac{1}{4} \dot{\lambda}^2 \right) - r^2 e^{-\lambda} \left(\frac{1}{2} \nu''^2 + \frac{1}{4} \nu'^2 - \frac{1}{4} \lambda' \nu' \right) = 0$$

, ... (12)

Although there are 64 different equations contained in (23) most of them are found to be identities—the independent equations being only the following four :

$$re^{-\lambda}T_{11}=\frac{\partial}{\partial r}T_{22}-\frac{1}{r}T_{22}+\frac{1}{3}r^2\frac{\partial T}{\partial r}, \quad . \quad . \quad . \quad (25)$$

$$re^{-\lambda}T_{14}=\frac{\partial}{\partial t}T_{22}+\frac{1}{3}r^2\frac{\partial T}{\partial t}, \quad . \quad . \quad . \quad . \quad . \quad (26)$$

$$\frac{\partial}{\partial r}T_{44}-\frac{1}{3}e^{\nu}\frac{\partial T}{\partial r}-\frac{\partial T_{14}}{\partial t}=\frac{1}{2}\dot{\lambda}T_{14}+\frac{1}{2}\nu'T_{44}-\frac{1}{2}e^{\nu-\lambda}\nu'T_{11}-\frac{1}{2}\dot{\nu}T_{14}, \quad . \quad (27)$$

$$\frac{\partial}{\partial r}T_{14}-\frac{1}{3}e^{\lambda}\frac{\partial T}{\partial t}-\frac{\partial T_{11}}{\partial t}=\frac{1}{2}\lambda'T_{14}+\frac{1}{2}e^{\lambda-\nu}\dot{\lambda}T_{44}-\frac{1}{2}\dot{\lambda}T_{11}-\frac{1}{2}\nu'T_{14}. \quad . \quad (28)$$

For a perfect fluid,

$$T_{\mu\nu}=(p+\rho)v_{\mu}v_{\nu}-pg_{\mu\nu}, \quad . \quad . \quad . \quad . \quad . \quad (29)$$

and

$$g^{\mu\nu}v_{\mu}v_{\nu}=1, \quad . \quad . \quad . \quad . \quad . \quad (30)$$

v_{μ} being the flow vector. For (10) the field equations give

$$\nu_2=0, \quad \nu_3=0, \quad T_{22}=pr^2, \quad T_{33}=pr^2\sin^2\theta \quad . \quad . \quad (31)$$

and from (29) and (30) we have

$$T=\rho-3p. \quad . \quad . \quad . \quad . \quad . \quad (32)$$

The equations (25) to (28) now become

$$-(p+\rho)v_1v^1=\frac{1}{3}\rho'r, \quad . \quad . \quad . \quad . \quad . \quad (33)$$

$$-(p+\rho)v^1v_4=\frac{1}{3}\dot{\rho}r, \quad . \quad . \quad . \quad . \quad . \quad (34)$$

$$e^{\nu}\left[p'+\rho'+\frac{r\rho''}{3}+\frac{1}{2}\nu'\left(p+\rho+\frac{2\rho'r}{3}\right)\right]=\frac{1}{3}e^{\lambda}[\dot{\rho}r+\frac{1}{2}\dot{\rho}r(3\dot{\lambda}-\dot{\nu})], \quad . \quad (35)$$

$$\frac{1}{3}\dot{\rho}r(\lambda'+\nu')=\dot{\lambda}(p+\rho+\frac{2}{3}\rho'r), \quad . \quad . \quad . \quad . \quad . \quad (36)$$

respectively. From (33) and (34) it follows that

$$(p+\rho)v_4v^4=p+\rho+\frac{1}{3}\rho'r, \quad . \quad . \quad . \quad . \quad . \quad (37)$$

and, on eliminating v_1 and v_4 with the help of (29), we get

$$\rho'\left[\rho'+\frac{3}{r}(p+\rho)\right]=\rho^2e^{\lambda-\nu}. \quad . \quad . \quad . \quad . \quad . \quad (38)$$

The problem now is to determine λ and ν in (10) subject to the five field equations, (13) to (16), and the four equations, (33) to (36). Actually (35) and (36) correspond to $l=1$ and $l=4$ respectively in (24) and are thus implicit in the field equations themselves. In practice it is convenient to use (35) instead of (14). From (37) and (15) we get

$$e^{-\lambda}=1-\frac{8\pi\rho r^2}{3}, \quad . \quad . \quad . \quad . \quad . \quad (39)$$

which is the same as (19). Hence for (10) the conditions (3) and (9) are satisfied by the same value of $e^{-\lambda}$. (13), (33) and (36) are satisfied by

$$8\pi(p + \frac{1}{3}\rho + \frac{1}{3}\rho'r) = \frac{v'}{r} \left(1 - \frac{8\pi}{3}\rho r^2\right). \quad (40)$$

The equations (16), (34) and (39) are mutually consistent.

The solution is ultimately provided by (39), which gives λ , and by (35), (38) and (40) which give p , ρ and v . All these four equations are found to be satisfied by Schwarzschild's internal solution for which ρ is constant. It is interesting to note that p does not appear explicitly in any one of the equations. Either $\rho' > 0$ or, as is clear from (38), $\rho' < 0$, in which case,

$$\rho' + \frac{3}{r}(p + \rho) \leq 0,$$

or

$$\rho' \leq -\frac{3}{r}(p + \rho).$$

Stability demands that ρ' be zero or negative. These limitations on density distributions indicate that only Schwarzschild's solution ($\rho' = 0$, $\dot{\rho} = 0$) is of physical interest under the restriction (9) on (10) when $R_{ij} \neq 0$. If $\rho' < 0$ and hence

$$\rho' \leq -\frac{3}{r}(p + \rho),$$

we have

$$M'r \leq -12\pi \int_0^r p r^2 dr \leq 0,$$

where

$$M = 4\pi \int_0^r \rho r^2 dr.$$

This case is of no physical interest since $M' \leq 0$.

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XIV. *The Fluorescence of Silver Halides at Low Temperatures.*
 Part I. *The Pure Halides* *.

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[Plates III.–VI.]

ABSTRACT.

Fluorescence emission spectra of AgCl, AgBr and AgI, believed to be characteristic of the pure solids, have been recorded at liquid nitrogen and liquid hydrogen temperatures. The spectra are all in the visible and lie just to the long wavelength side of the absorption bands of the respective halides. No resolution of the spectra was observed down to the lowest temperatures; no pure halide specimen emitted any phosphorescence or thermal afterglow. The two different structures of AgI capable of existence at ordinary and low temperatures (wurtzite and zincblende) gave slightly different emission spectra.

The temperature at which the fluorescence just became visible was about 180° K. for AgCl and AgI, but only 77° K. for AgBr. Excitation of the fluorescence could be effected by any wavelength which the halide was capable of absorbing.

All three halides emitted an extra band in the red after being exposed to light action at ordinary temperature, or slightly decomposed by heat treatment, so as to give a dispersion of free silver in the halide. Large quantities of impurity (~1–3 M. per cent) were required in order to alter appreciably the characteristic emission of the basic silver halide.

The low-temperature fluorescence of the pure halides is believed to be due to the direct recombination of excited electrons with positive holes with the emission of visible radiation, instead of the emission of thermal quanta as at higher temperatures.

I. INTRODUCTION.

THIS work was prompted by Meidinger's investigation of the low-temperature fluorescence of suspensions of silver chloride, bromide, iodide, and bromiodide in gelatin, prepared in the manner of photographic emulsions (Meidinger 1939, 1940). It was uncertain whether the pure silver halides would fluoresce in the absence of gelatin: Randall observed that silver chloride shows a bright blue-green fluorescence at 77° K., but thought that some impurity was responsible. We find that all three halides fluoresce strongly in the pure state at a sufficiently low temperature, that is, they show the so-called "fundamental" or "lattice" emission.

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Until quite recently it was thought that pure solids, apart from manganese, rare-earth, and uranyl compounds having screened incomplete shells of electrons, did not show fluorescence (Seitz 1939; Mott and Gurney 1940). Fluorescence in the pure state, however, has been reported for NaCl, KCl, NaBr, KBr, (Kudriavzewa 1934) ZnS, ZnO and CdS (Kröger 1940), and on theoretical grounds one expects pure substances in general to fluoresce at low enough temperatures: what calls for explanation is not so much the fact of fluorescence as the mechanism by which it is quenched at high temperatures. The main interest of the present work lies in the finding that AgCl, AgBr and AgI have to be added to the above list. All these substances show a low-temperature fluorescence band lying on the long-wavelength flank of the absorption band.

The present paper (Part I.) is concerned with the individual silver halides: Part II. will deal with mixed silver-halide crystals. The results to be described consist mainly of emission spectra, though some observations were made of excitation spectra and the temperature-variation of the intensity of emission. Except where otherwise stated, all results were obtained at liquid-nitrogen temperature (77° K.).

2. SPECIMEN PREPARATION AND EXPERIMENTAL TECHNIQUE.

(i) *Specimen preparation.*

The specimens were prepared using distilled water and A.R. grade, or purer, reagents, *e. g.* the AgNO_3 employed in photographic emulsion manufacture which is purer than A.R. grade. In the precipitations 0.1 M. solutions were employed, as the washing of the precipitate is inefficient with concentrated solutions (Frankenburger, 1923). During the preparation and handling, Kodak Wratten Series "O" safelights were used for darkroom illumination: occasionally preparation was carried out in darkness. No exposure to actinic light was allowed until the specimen was at low temperatures.

Usually equivalent amounts of silver nitrate and metal halide solutions were mixed, *e. g.* 50 ml. 0.1 M. KCl and 50 ml. 0.1 M. AgNO_3 (yielding "equivalent crystals"). "Excess Ag" specimens were made by pouring the halide solution into an AgNO_3 solution containing 10 M. per cent more than the equivalent quantity of solute, thus ensuring an excess of silver ion throughout the precipitation. The converse procedure was employed to make "excess halide" specimens. All precipitates, particularly the "excess" ones, were thoroughly washed and dried before testing.

To eliminate the possible influence of inclusions of solution in the precipitate certain samples were shaken in water for some hours. In the cases of AgCl and AgBr this yielded large grains of about 1 mm. in diameter, not single crystals but hard compact aggregates, which, according to Frankenburger, have no inclusions. Further special preparations of various specimens will be described later, where appropriate.

(ii) *Experimental technique.*

The specimens were usually loaded into the lower closed end of a length of $\frac{3}{8}$ -inch glass tubing, which was immersed in a transparent Pyrex or quartz Dewar flask containing liquid nitrogen. They were excited by the radiation of a 125 w. mercury high-pressure arc transmitted by a Wratten 18A filter (3130 Å.-4047 Å.). Excitation by the Hg lines transmitted by a 10 cm. thickness of a compound solution of 41.5 g. $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ and 145 g. $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ in 1 litre of distilled water (2480 Å.-3341 Å.) (Bowen, 1935) was found to give the same results. In this case specimens were mounted as layers on the lower end of a glass strip, a thin layer of gelatin being employed as adhesive. Specimens, immersed in the quartz Dewar flask of liquid nitrogen, could then be irradiated without the exciting radiation having to pass through glass.

The fluorescent light was focused on to the slit of a Hilger Medium quartz spectrograph (with occasional recourse to the Hilger Constant Deviation glass instrument), and the spectrum recorded on Kodak P.1200 or P.1500 plates. A Wratten No. 2 or 2A filter was mounted at the condensing lens to eliminate the ultra-violet radiation scattered in the direction of the spectrograph. The glass condensing lens eliminated the shorter wavelength ultra-violet when the Bowen filter was employed. Direct Hg spectra were always recorded with the fluorescence spectrograms, for calibration purposes. With the brightest specimens and a slit width of $\frac{1}{10}$ mm. an adequate exposure time was 1-2 minutes. Precisely the same technique was employed for recording the emission of specimens at liquid hydrogen temperature (20° K.).

Certain spectra were examined with the aid of a photomultiplier cell. The emission of the specimen was allowed to pass right through the quartz spectrograph, at the farther side of which it was further dispersed by a large replica grating and brought into focus; the linear extension of the spectrum was increased by a factor of three. The photomultiplier cell with a narrow slit in front of its cathode, was moved along a graduated scale in the plane of the spectrum, and current readings were taken at various regular intervals. With the help of line-spectrum calibration of the scale, and the spectral-sensitivity curve of the photomultiplier cell, it was possible to obtain a curve of relative intensity against wavelength for the fluorescent light. This was much more convenient than correcting for spectral sensitivity of the panchromatic plates employed in the photographic recordings.

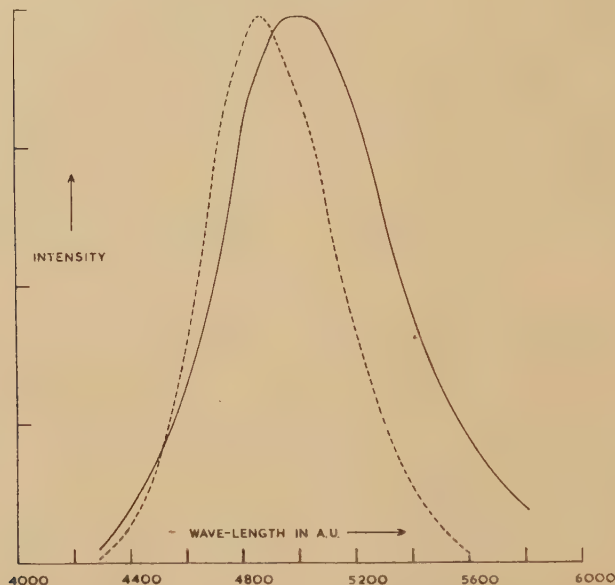
The excitation of various Hg lines and groups were observed by dispersing radiation from a high-intensity Hg source with the dispersing system employed with the photomultiplier. A small quartz Dewar flask containing the specimen in a tube immersed in liquid nitrogen was placed in the plane of the Hg spectrum and the effects of separate lines observed through a grating, which dispersed at right angles to the direction of dispersion of the exciting system.

3. SILVER CHLORIDE.

(i) *Emission spectra.*

All precipitated specimens at 77° K. emitted a broad structureless band extending from 4350 Å. to 5800 Å. (Pl. III., fig. 1, *a*). The colour of the fluorescence was blue-green. Measurements with the photo-multiplier arrangement showed that it was a single smooth band with a peak at 5000 Å. (fig. 1). The extent and position of the band agrees with

Fig. 1.



The spectral distribution of fluorescence of AgCl at low temperatures. Intensity in arbitrary energy units :

Solid curve—specimen at 77° K.

Dashed curve—specimen at 145° K.

Ordinates of latter curve adjusted to give same intensity at maximum, so as to show more clearly the shift of the band to shorter wavelengths on increase of the specimen temperature.

Randall's results (Randall 1939). That it cannot be ascribed to any impurity in the precipitating reagents seems clear from the fact that specimens precipitated from eleven different metal halides (*e.g.* NH_4 , Fe, Co, Ni, Mn, Ca) and several different specimens of AgNO_3 and Ag_2SO_4 gave identical spectra. Some examples are shown in Pl. III., fig. 1, *b*, to *e*.

To eliminate the possibility that structural defects in the precipitate were responsible for the low temperature emission, single crystals of AgCl (1–2 mm. in size) were grown from ammonia solution and examined. Their low-temperature fluorescence was just as intense as that of the

precipitates. It was still possible that defects associated with an excess of silver were leading to the observed emission, but this was discounted by the fact that annealing the large crystals at 400°C . for five hours in an atmosphere of chlorine, and then cooling slowly to room temperature (which would also tend to eliminate structural defects) gave specimens which were even more strongly fluorescent than before the annealing treatment. A specimen prepared by the action of pure, dry chlorine on Hilger "Specpure" silver gave an emission spectrum identical with those already recorded.

If a specimen was melted in the open air, either in a platinum or porcelain crucible, so that, in the reducing atmosphere of the Bunsen flame, slight decomposition took place, with the formation of free silver, the emission was always found to include a band in the red ($5800\text{ \AA}$. to $6450\text{ \AA}$. Pl. III., fig. 1, *f* and *g*). This red band could also be induced by a short exposure of the specimen to ultra-violet radiation at ordinary temperatures, which led to the formation of "print-out" silver. Careful tests showed that the red emission, which was observed with all halide specimens after appropriate preparation or treatment, could only be excited by radiation which was absorbed by the halide, *i. e.* there was no specific excitation band of the silver impurity. It was induced more readily in an "excess silver" specimen. The red emission is obviously associated with the silver excess, but whether it is due to small specks or atoms of silver acting as impurity centres, or to the formation of F-centres, is at present an open question. Melts showing the red fluorescence also gave a weak red phosphorescence and a thermal afterglow occurring in two bursts, the first having a green and the second a red colour.

(ii) Impurity activation.

The results of these experiments are important in considering the validity of the claim that pure AgCl is fluorescent at low temperatures. Mn, Mg, Cu and Pb (as chlorides) were incorporated in the AgCl as impurities (by melting in halogen atmosphere), in quantities ranging from 10^{-4} M. per cent to 5 M. per cent. It was found that comparatively large quantities of impurity ($\sim 1\text{--}3$ M. per cent) were required in order to alter the normal AgCl emission appreciably. Such changes as occurred usually consisted of an extension of the emission towards the red; the emission spectogram of a specimen containing 5 M. per cent Mg is shown as an example (Pl. III., fig. 1, *h*). Specimens containing ~ 1 M. per cent Mn showed a fairly strong red emission band to be ascribed to the Mn impurity (Pl. III., fig. 1, *i*); at 5 M. per cent Mn the normal AgCl emission had practically been suppressed and replaced by a strong red Mn band ($5920\text{ \AA}$.– $6450\text{ \AA}$.; Pl. III., fig. 1, *j*).

The specimens which contained ~ 1 M. per cent Mn were particularly interesting in that their colour of emission changed from green to red as the intensity of excitation was reduced, and showed a change in the same

direction as their temperature was raised. This phenomenon is analogous to that observed in the case of $\text{ZnS} + \text{Cu}$, or $\text{ZnS} + \text{Mn}$ (Gisolf and Kröger, 1939), and can be explained by the mechanism put forward by Schön (1942) and Klasens (1946). It depends essentially on the fact that the energy gap between the ground state of the AgCl centres and the $3p$ band of AgCl is less than the corresponding gap for the Mn centres. An analysis based on this and certain other simplifying assumptions (for which reference must be made to the original sources) leads to expressions which are in qualitative agreement with the phenomena observed. Perhaps the most interesting fact to be deduced from the above observations is that positive holes are mobile in AgCl at low temperatures, at least over a distance of a few lattice spacings.

(iii) *The influence of temperature.*

Measurements with a copper-constantan thermocouple have shown that the fluorescence of AgCl commences at a temperature of 180°K . From this temperature down to 20°K . the emission band (or rather the peak) moves over towards longer wavelengths. At 150°K . the emission appears blue in colour, at 77°K . blue-green, and green at 20°K . This is well illustrated by the three spectrograms shown in Pl. III., fig. 2, *a-c*, recorded at the three specimen temperatures noted above. (The emission at 20°K . was recorded with the glass spectrograph and thus the spectrogram is on a different scale from the other two.) The shift to shorter wavelengths with increasing temperature is also illustrated in fig. 1.

(iv) *Excitation.*

Tests with the arrangement described in § 2, (ii), have shown that AgCl is strongly excited by all Hg lines in the ultra-violet region, but only weakly by the Hg $4047 \text{ \AA}$. line. The absorption edge of AgCl is at about $4300 \text{ \AA}$. and it is thus apparent that the fluorescence of AgCl is excited by all wavelengths which it absorbs. The emission excited by wavelengths in the range $2480 \text{ \AA}.$ – $3130 \text{ \AA}$. was identical in spectral distribution with that excited by the longer ultra-violet wavelengths.

4. SILVER BROMIDE.

(i) *Emission spectra.*

Ordinary precipitates and open-atmosphere melts of AgBr at 77°K . showed a faint emission band in the red extending from $5700 \text{ \AA}$. to $6450 \text{ \AA}$. (Pl. IV., fig. 3, *a* and *b*). This red band was strongest in the slightly decomposed melts and the "excess silver" precipitate. Spectroscopic tests with Kodak Infra-Red Extra-Rapid plates showed that it did not appreciably extend beyond $6450 \text{ \AA}$. The red emission was suspected of being due to a silver impurity in the various specimens, and to test this, a specimen free from silver was prepared by melting some AgBr in an atmosphere of bromine and then quenching it in distilled water. It

was found to be completely non-fluorescent at 77°K . When it had been allowed to "print out" at ordinary temperatures for a few seconds, however, the red emission was again observable at low temperatures. This is fairly conclusive evidence that the red emission is due to the presence of silver.

The "excess bromide" specimen at 77°K . gave an additional faint emission band in the green (Pl. IV., fig. 3, c) and it was believed that this represented the emission of pure AgBr, in analogy to the blue-green emission of AgCl, but that a much lower temperature was required in order to observe it at high intensity. This belief was found to be justified when observations were made at a specimen temperature of 20°K . AgBr gave a very strong green emission in a single band extending from $4720\text{ \AA}$. to $5375\text{ \AA}$. with a peak at $5050\text{ \AA}$. This is shown in Pl. IV., fig. 3d, along with the red "silver" band which appeared with quite high intensity at 20°K . We believe the green emission band to be characteristic of pure AgBr, although it must be admitted that there is not such an overwhelming weight of evidence in favour of this claim as in the case of AgCl.

(ii) *Impurity activation.*

The most striking result in this section, but one which properly belongs to Part II., was the effect of precipitating small quantities ($\sim 5\text{ M. per cent}$) of AgI in AgBr so as to form mixed crystals. Such specimens showed a very strong green emission, the spectrum of which was a single band extending from $5150\text{ \AA}$. to $6000\text{ \AA}$. with a peak at $5500\text{ \AA}$. (Pl. IV., fig. 4, a). The position agrees with that recorded by Meidinger for the emission of silver bromo-iodide emulsion layers. We believe, for reasons to be given later, that the emission of such specimens is seated in the iodide ion, and that the green band is not a "sensitized" bromide band.

Evidence supporting the latter contention is provided by the fact that inclusions of other mono- and divalent halides, *e. g.*, CuCl, CuCl₂, PbCl₂, PbBr₂, MgCl₂, to the extent of 5 M. per cent, had only very weak activating effects. In general they gave specimens showing weak emission bands in the red and yellow. (The red bands were not due to a silver impurity, as the inclusion of impurity by melting was carried out in a bromine atmosphere.) Some examples of the spectra are shown in Pl. IV., fig. 4, b-d.

5. SILVER IODIDE.

(i) *Emission spectra.*

The essential features of an AgI emission spectrum are well illustrated by P. ., fig. 5, a, the specimen in this case being prepared by the action of iodine vapour on spectroscopically pure silver. The main band extends from $4400\text{ \AA}$. to $4600\text{ \AA}$.; the narrow short wavelength band was of variable position, but in the case illustrated is situated at $4220\text{ \AA}$. A red band, in a similar position to the "silver" bands of AgCl and AgBr,

could be induced by exposure of the AgI at ordinary temperatures. Almost all precipitates emitted this red band: it was particularly strong in "excess silver", and aged, precipitates (Pl. V., fig. 5, *b* and *c*). Some specimens also emitted a faint band in the green (Pl. V., fig. 5, *c* and *d*), which was assigned to some impurity, since it was not present in the emission of the purest specimen prepared by the action of iodine on silver, or in the emission of the majority of precipitates prepared with alternative reagents.

A puzzling feature of the first recordings of emission spectra of various AgI specimens was the manner in which the positions of the main band and narrow band altered, depending on the conditions of precipitation, *e. g.*, the narrow band was emitted at shorter wavelengths in the case of "excess iodide" specimens (Pl. V., fig. 5, *e*). It was later realized that these variations were almost certainly due to the fact that at ordinary temperatures AgI is precipitated as a mixture of wurtzite-type (hexagonal) and zincblende-type (cubic) structures (Wilsey 1923), and that different specimens contained different proportions of the two structures. X-ray diffraction patterns confirmed this surmise, and so extensive efforts were made to prepare AgI specimens of one single structure. The methods employed for obtaining the wurtzite structure were:—

(a) Precipitation of AgI dissolved in concentrated HI solution by slow addition of ethanol (Helmholz 1935).

(b) Rapid precipitation of AgI by dilution of a concentrated solution of AgI in KI (Bloch and Möller 1931).

(c) Slow cooling of an AgI melt (Bloch and Möller 1931).

(d) Slow crystallization of AgI from a dry piperidine solution by absorption of atmospheric water vapour by the latter. This method yielded soft aggregates of external hexagonal form, but which were opaque and easily crumbled to a mass of small crystals.

For obtaining the zincblende structure, the methods used were:—

(e) Rapid precipitation of AgI by dilution of a concentrated solution of AgI in AgNO_3 (Bloch and Möller 1931, Kolkmeijer and Hengel 1934).

(f) Pulverization of any hexagonal specimen, *e. g.* pieces of slow cooled melt of (c) or the soft aggregates of (d), in an agate mortar and pestle.

Debye-Scherrer powder diagrams showed that in no case was a specimen obtained whose structure was completely one or the other type, but some approached 90 per cent structural purity. From these it was possible to distinguish the features characteristic of the emissions of the two different structural types. They are particularly well illustrated by Pl. ., fig. 6, *a* and *b* which show the emission of a piece of slow cooled melt and that of a predominantly cubic precipitate prepared by method (e). The narrow band is at a shorter wavelength in the case of the hexagonal specimen, while the main band is at longer wavelengths. The latter fact is even better illustrated by the two low-exposure spectrograms shown in

Pl. V., fig. 6, *c* and *d* of the emission of predominantly cubic and hexagonal precipitates. A further comparison of predominantly cubic and hexagonal precipitates is made in Pl. V., fig. 6, *e* and *f*. It should be noted how intense the red "silver" bands are in the emission of the cubic precipitates; their preparation in all cases involved a heavy excess of silver.

The change over in emission characteristics when a specimen is converted from hexagonal to cubic by method (*f*) is illustrated by Pl. V., fig. 7. The first spectrogram (Pl. V., fig. 7, *a*) is that of the fluorescence of predominantly hexagonal crystals prepared by method (*d*), the second and third (Pl. V., fig. 7, *b* and *c*) those of the same crystals after being ground for 10 and 20 minutes respectively. The growth of the narrow band at longer wavelengths and the shift of the main band towards shorter wavelengths are easily visible. X-ray powder diagrams confirmed a general change-over from hexagonal to cubic structure.

A careful study of all spectrograms and the X-ray powder diagrams of the corresponding specimens showed that all the variations in spectral emission exhibited were due to the various proportions of the two different structural types in the various specimens. For instance, the specimen precipitated in excess iodide solution which gave a narrow band at shorter wavelengths (Pl. V., fig. 5, *e*) than did other precipitates, was found to be predominantly hexagonal in structure.

A puzzling feature of the low-temperature emission of AgI is the fact that the narrow short wavelength emission band falls within the (low-temperature) absorption band of the halide. This is illustrated by Pl. VI., fig. 8, *a-c* which contrasts the emissions of predominantly cubic and hexagonal specimens (fig. 8, *a* and *c*) with the absorption spectrum of a mixed specimen (fig. 8, *b*) (tests showed that the wavelength of the absorption edge was sensibly independent of the structure of the AgI specimen). We believe that the main emission band of AgI, and the emission bands of AgCl and AgBr, are due to the direct recombination of the excited electron with a positive hole at low temperatures, this process having a relatively low probability at higher temperatures compared with the probability of radiationless recombination. At the present moment, however, we cannot suggest any mechanism which explains the emission of the narrow AgI band, or why it is emitted in a spectral region where the absorption coefficient is high ($\sim 10^5 \text{ cm.}^{-1}$) (Schell 1911).

Its intensity, however, does appear to be controlled by the absorption of the halide as it was found that the narrow band was much more intense from a specimen which had been sedimented into a compact layer, than from the same specimen mounted in a tube as a loose, fine powder. This is illustrated by Pl. VI., fig. 9, *a* and *b*. The reason why the self absorption should be less in the first case is not at all obvious, however. The intensity of the narrow band was particularly high in the case of emissions from smooth surfaces of melts, and was much reduced when such specimens were broken down with little change in structure. It thus appears that the narrow band emission cannot be assigned to surface ions.

(ii) *The influence of temperature.*

The fluorescence of hexagonal specimens became visible at about 195°K. and that of cubic specimens at a slightly lower temperature. At 77°K. hexagonal specimens showed an appreciably higher fluorescence efficiency. Pl. VI., fig. 10 compares the emissions of a mixed AgI specimen at 77°K. (a) and 20°K. (b), identical exposure conditions being employed in each recording. It will be seen that the fluorescence is much more intense at the lower temperature, and that the spectrum has shifted and extended towards shorter wavelengths. The extension towards shorter wavelengths is probably connected with the retraction of the absorption edge on reduction of the temperature. The narrow bands do not appear to be shifted, and have undergone little change in intensity.

(iii) *Excitation.*

All Hg lines up to $4047\text{ \AA.}$ were found to excite specimens of AgI strongly, but not lines beyond this wavelength. The absorption edge of AgI at low temperatures is at $4250\text{ \AA.}$ and thus, as in the case of AgCl, we see that fluorescence is stimulated by all wavelengths which are capable of being absorbed. This result is indeed to be expected if the fluorescence observed is characteristic of the pure solid.

6. PHOTOGRAPHIC EMULSIONS.

Some attention was paid to the fluorescence of photographic emulsions at low temperatures. The emission spectra corresponded to a simple superposition of the emissions of their silver-halide contents and gelatin. The latter, investigated separately, was found to show a blue fluorescence at both ordinary and low temperatures: the spectrum extended over the whole of the visible region. It also showed a moderately strong phosphorescence at low temperatures, which was reproduced in the emulsions.

No differences in emission were observed between dye-sensitized and unsensitized emulsions of otherwise identical composition. Photographic desensitizers were also found to have no appreciable influence on the fluorescence. It also appeared that emulsion impurities, such as silver sulphide specks on the grain surfaces, and silver-gelatin complexes, etc., had no important activating or de-activating effects.

Meidinger has reported that the efficiency of fluorescence of bromo-iodide emulsions (96 per cent AgBr, 4 per cent AgI) depends strongly on grain size at a given temperature. At 77°K. a coarse-grain emulsion gave a strong fluorescence having a quantum efficiency of about 0.9, a series of finer-grain emulsions gave progressively lower efficiencies, and a Lippmann-type emulsion of very fine grain showed no fluorescence at all. We have been unable to confirm this result: we have examined a number of bromo-iodide emulsions of various grain sizes, including a specially prepared series having the same constitution and a wide range of grain

sizes, and several transparent Lippmann-type emulsions, and all showed about the same high intensity of fluorescence. A speculative explanation of Meidinger's results on fine-grain emulsions would be that he employed a method of precipitation that enabled the relatively insoluble AgI to precipitate before the AgBr with little formation of genuine mixed crystals.

The fact that we recorded identical spectra for the emissions of bromo-iodide precipitates and bromo-iodide emulsions (except for the weak overlying gelatin emission spectrum in the latter case) shows that the green fluorescence of the latter is not due to activation of the bromo-iodide by silver sulphide specks, as has been suggested by Vassy and Vassy (1948).

7. CONCLUSIONS.

The experimental results which have been described show that the silver halides are fluorescent in the pure state at low temperatures. Besides the evidence provided by the many alternative preparations of the halides, the position of the emission band of each halide on the flank of its absorption band suggests that the fluorescence is of the "fundamental" or "lattice" type. We can explain our results in terms of the following simple model. If the system in the excited state (reached directly by absorption, or after the electron has spent some time in the conduction band) receives sufficient thermal energy to raise it from the minimum of the state to a point where it can cross over to a high vibrational level of the ground state, it will accomplish the return to the bottom of the ground state with the emission of vibrational quanta. At low temperatures however, where the probability per unit time of the above process has fallen to a low or negligible value, the excited electron will return directly to the ground state (recombination with a positive hole) with the emission of radiation. It will be shown in Part II. how the results for the variation of fluorescence efficiency of silver bromo-iodide fit in with the simple explanation given above.

We expect that careful investigation will show that many pure crystals exhibit a low-temperature fluorescence analogous to that of the silver halides. We have observed a fluorescence of the cuprous halides which is probably of this type. Our interest was centred on the silver halides in the hope that information would be obtained of some use in photographic latent-image theory. It is known that a developable latent image can be formed in a photographic emulsion by exposure at or below liquid nitrogen temperature; it is supposed that the photoelectrons released during the exposure are trapped mainly in shallow traps, and released on warming up, when also the ionic movements necessary for latent-image formation can take place (Berg 1939). It has been found that in all cases there is a fall in sensitivity at low temperatures as compared with that at ordinary temperatures. Some of this fall is no doubt due to the wastage of the energy of the exposure as fluorescence.

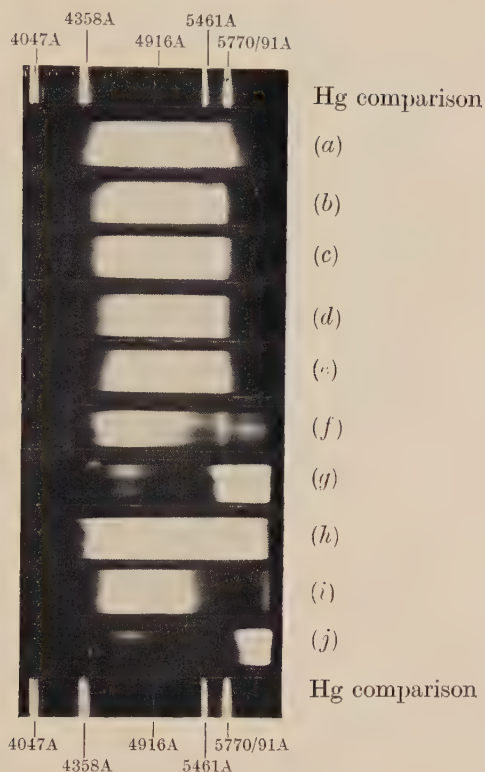
ACKNOWLEDGMENTS.

We are indebted to Professor F. E. Simon, C.B.E., F.R.S., of the Clarendon Laboratory, Oxford, for his assistance in enabling us to carry out the observations at liquid hydrogen temperature. Our thanks are due also to Mr. A. H. Fox of these laboratories who recorded many of the X-ray powder diagrams of our specimens, and Mr. D. J. Yates who rendered assistance in some of the experiments.

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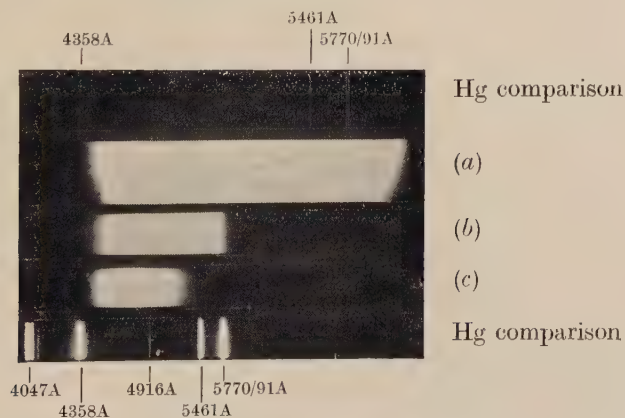
FIG. 1.



Emission spectra of silver chloride specimens.

- | | |
|---|--|
| (a) AgCl from KCl + AgNO ₃ . | (f) AgCl <i>slightly decomposed</i> (free Ag present). |
| (b) " " CaCl ₂ + AgNO ₃ . | (g) AgCl <i>heavily decomposed</i> (" " "). |
| (c) " " MgCl ₂ + AgNO ₃ . | (h) AgCl + 5 mol. per cent MgCl ₂ . |
| (d) " " CoCl ₂ + AgNO ₃ . | (i) AgCl + 1 mol. per cent MnCl ₂ . |
| (e) " " MnCl ₂ + AgNO ₃ . | (j) AgCl + 5 mol. per cent MnCl ₂ . |

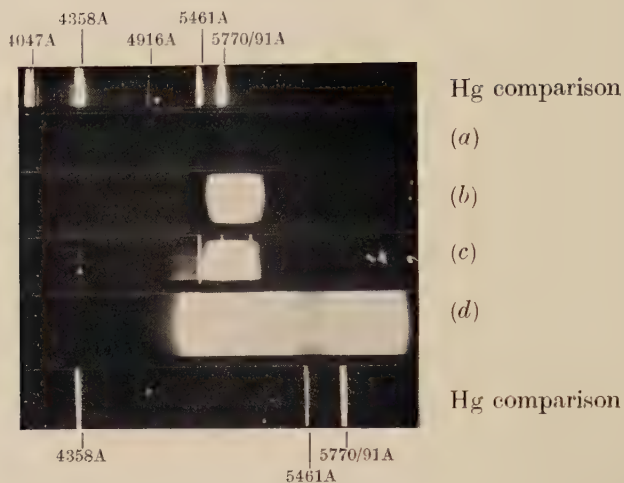
FIG. 2.



Emission spectra of silver chloride at various temperatures.

- (a) 20° K. (*glass spectrograph*). (b) 77° K. (c) 150° K.

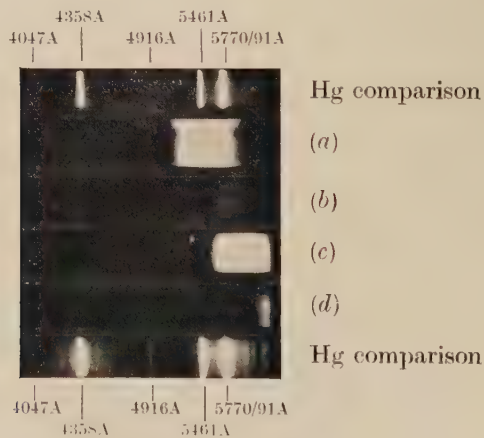
FIG. 3.



Emission spectra of silver bromide specimens.

- (a) "Normal" precipitate (77° K.).
- (b) Slightly decomposed melt (77° K.).
- (c) "Excess bromide" precipitate (77° K.).
- (d) "Normal" precipitate (20° K. ; glass spectrograph).

FIG. 4.



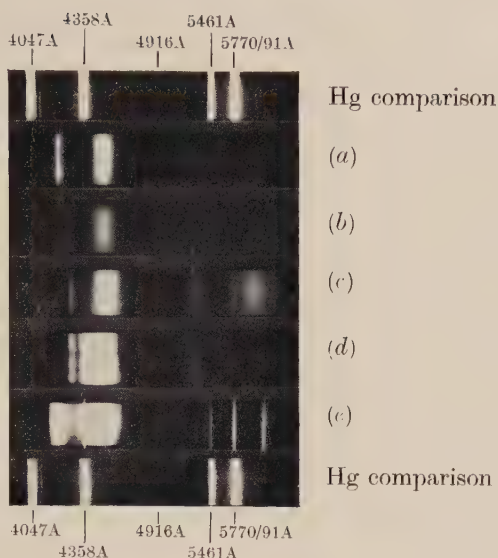
Impurity activated silver bromide.

- (a) $\text{AgBr} + 5 \text{ mol. per cent AgI}$.
- (b) $\text{AgBr} + 5 \text{ mol. per cent PbCl}_2$.
- (c) $\text{AgBr} + 5 \text{ mol. per cent MgCl}_2$.
- (d) $\text{AgBr} + 2 \text{ mol. per cent MnCl}_2$.

FIG. 5.

Emission spectra of AgI specimens.

- (a) From action of I_2 on Ag.
 (b) "Excess silver" specimen.
 (c) "Excess silver" specimen, emitting band in green.
 (d) From $HI + AgNO_3$, emitting band in green.
 (e) "Excess iodide" specimen.



Hg comparison

FIG. 6.

Comparison of the emission spectra of wurtzite (hexagonal) and zincblende (cubic) specimens of AgI.

- (a) Hexagonal AgI; slow cooled melt.
 (b) Cubic AgI; rapid dilution of concentrated solution of AgI in $AgNO_3$.
 (c) Hexagonal precipitate of AgI.
 (d) Cubic precipitate of AgI.
 (e) Hexagonal precipitate.
 (f) Cubic precipitate.
- } Low exposures.
 } Different preparations to those noted above.

Hg comparison

FIG. 7.

The change in emission spectrum of AgI on change of structure.

- (a) Hexagonal AgI prepared from piperidine solution.
 (b) Same specimen after partial conversion to cubic structure by grinding.
 (c) Further conversion to cubic structure.

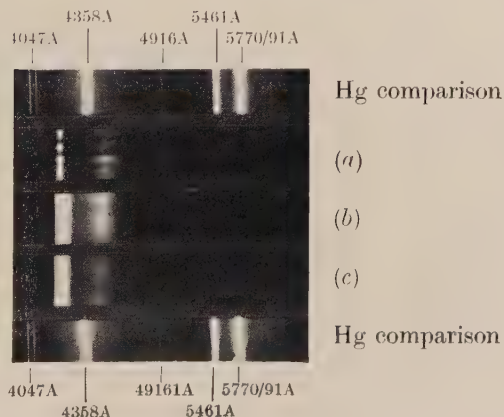
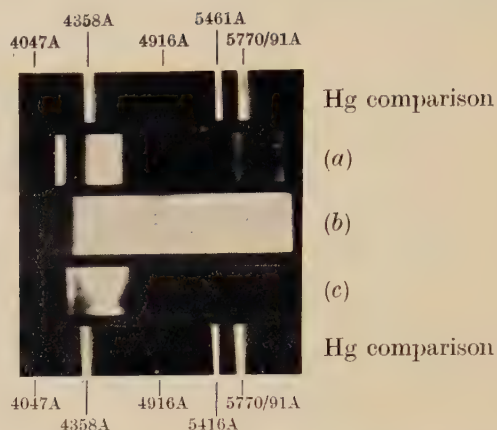


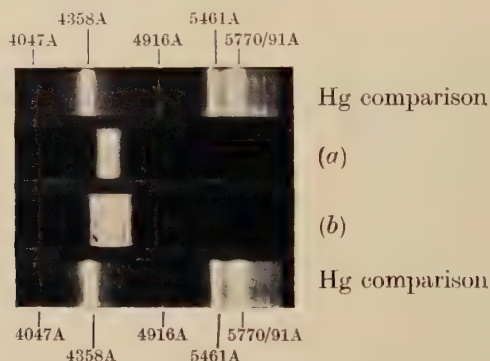
FIG. 8.



Comparison of the emission spectra of cubic and hexagonal specimens with the absorption spectrum of AgI at 77° K.

- (a) *Predominantly hexagonal precipitate.*
 (b) *Absorption spectrum of mixed precipitate.*
 (c) *Predominantly cubic precipitate.*

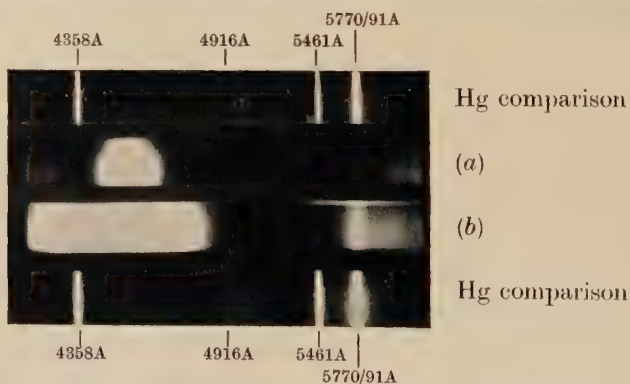
FIG. 9.



Comparison of emission spectra from a compact layer and a loose powder of a particular AgI specimen.

- (a) *Compact layer.*
 (b) *Same specimen in loose powder form (longer exposure employed in recording).*

FIG. 10.



Emission spectra of an AgI specimen at 77° K. and 20° K.

- (a) 77° K. (b) 20° K. (same exposure conditions as in (a)).

Glass spectrograph employed for recording the spectra.

XV. *Nuclear Transmutations Produced by Cosmic-Ray Particles of Great Energy.*—Part III. *Nature of the Shower Particles.*

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SUMMARY.

A new method of measuring the scattering of charged particles in their passage through photographic emulsions has been developed. It has been employed to determine the mass of charged particles emerging from nuclear "explosions" produced by cosmic radiation. Of the mesons among the "shower" particles, produced in these explosions with momentum less than about 180 MeV./c, it is shown that at least 90 per cent are π -particles; and that less than 5 per cent, and possibly none, are μ -particles, electrons or other particles of small mass. If mesons of greater mass are sometimes created in nuclear interactions with an energy less than 300 MeV., they must be produced with a frequency less than 1 per cent of the protons and less than 5 per cent of the π -particles. The observations therefore prove that the great majority of the charged particles created in nuclear interactions are π -particles.

The greatly increased rate of measurement with the new method and the fact that it allows the determination of the scattering of particles of much greater energy than has been possible hitherto will enable a detailed study of the nuclear transmutations produced by protons and α -particles with energies in the interval from 10^9 to 10^{10} eV. to be made.

INTRODUCTION.

IN Part II. of the present series of papers (Camerini *et al.*: 1949), which will be referred to as (II.), it was shown that, in favourable cases, it is possible to determine the rest-mass and the energy of fast-charged particles, emitted during the explosive disintegration of nuclei, by observations of the grain-density in the tracks and the deviations in them due to multiple Coulomb scattering. The essential principles of the methods employed for measuring the scattering have been described by Goldschmidt-Clermont *et al.* (1948) and by Davies *et al.* (1949).

* Communicated by Professor C. F. Powell, F.R.S.†

† It had been intended that Part III. of the present series of papers should contain a discussion of the experimental material given in Parts I. and II. The rapid development of the methods discussed in Part II.—and, in particular, the improvements in the scattering method described by Mr. Fowler in the present paper—allowed us, however, to obtain a more detailed insight into many features of the nuclear disintegrations produced by protons and α -particles of great energy. It therefore seemed desirable to make a more extensive series of investigations, and the final discussion will be postponed to a later paper. (C. F. P.).

It was pointed out in (II.) that the new method is similar in principle to that employed in experiments with Wilson chambers operated in magnetic fields. The average deviation in a track per unit length, $\bar{\alpha}$, gives a measure of the quantity $p\beta/Z$ for the corresponding particle, where p is its momentum, Ze its charge, and β the ratio of the velocity of the particle, v , to that of light, c . On the other hand, if the charge of the particle is known, the grain-density in its track gives a measure of its velocity—and thence the corresponding value of β . The two observations on the same track therefore allow both the mass and the velocity of the particle to be determined if its energy lies in a particular range of values; *viz.*, that its kinetic energy is less than $0.6 mc^2$, where m is the rest-mass, and greater than ~ 15 MeV. The method has the advantage that it is possible to measure the specific ionization of a particle of the cosmic radiation, by observations on the "grain density" in its track in a photographic emulsion, with a much greater precision than by "drop-counts" from photographs taken with "counter-controlled" Wilson chambers. Further, in favourable circumstances, it appears to be possible to determine the quantity $p\beta/Z$, by scattering measurements, with an accuracy comparable with that commonly achieved in experiments on the magnetic deflection of charged particles of the cosmic radiation.

The importance of the new method lies in the fact that it greatly extends the field of application of the photographic method. Hitherto, using this method of detection, determinations of mass have been confined to particles of low energy which reach the end of their range in the emulsion. The new method removes this restriction and, within certain limits, allows us to determine the mass and energy of particles, irrespective of whether or not they escape from the emulsion.

Whilst the early measurements, described in (II.), showed the potentialities of the method, the determination of the scattering parameter, $\bar{\alpha}$, was arduous, for it involved plotting the individual grains along a track from an image thrown on a screen by means of a projection microscope. This feature placed a limit on the field of application of the method: for with the apparatus at our disposal, an extensive analysis, made desirable if observations of great statistical weight were to be obtained, would have occupied some years. It therefore became desirable to develop simplified methods; and we have found that the following, which employs microscopes of conventional design, has the advantage of greatly increasing the rate of measurement, without an appreciable loss in precision, in addition to extending the range of values of the energy of particles which can be determined.

DETERMINATION OF THE SCATTERING PARAMETER.

In order to determine the scattering parameter, $\bar{\alpha}$, for a given track, the plate is placed on the mechanical stage of the microscope, so that the track is approximately parallel to one of the lines of motion of the stage,

say the X-axis. The point, y_1 , at which the image of the track intersects a hair-line in one of the eye-pieces, is determined by means of an eye-piece scale. The X-motion of the stage is then moved through a standard distance, say $100\ \mu$, and a reading taken of the new position, y_2 , of the image of the track relative to the eye-piece graticule. The operations are repeated along the entire length of the track.

The first differences, $S_1 = y_1 - y_2$, $S_2 = y_2 - y_3$ etc. give a measure of the inclination i_1 , i_2 , etc. of the successive chords in the track—and the second differences, $S_1 - S_2$, $S_2 - S_3$, etc. the deviations, D_1 , D_2 , etc. between successive chords. The mean value of $|D|$, $\frac{\sum_n |D|}{n} = \bar{D}$, taken without regard to sign, gives a measure of the scattering parameter, $\bar{x}$, from which the quantity $p\beta/Z$ can be evaluated.

For the successful application of the method, it is necessary that any apparent deviations in the track due to mechanical imperfections of the stage motions shall be compared with the deviations due to scattering. It has been found that satisfactory performance in this respect is given by Type M4000 microscopes by Cooke, Troughton and Simms. These instruments can be fitted with a kinematic stage provided with micrometer adjustments on both the x - and y -motions. It appears to be difficult to make a simple test of the performance of a given stage without special optical devices, but observations on the tracks of the particles with great momentum suggest that, when in good adjustment, any imperfections in the motion of the stage lead to errors which are not greater than those involved in reading the point of intersection of the image of the track and the eye-piece graticule.

The results of a characteristic series of measurements on part of a track of length 8 mm. is shown in Table I. In this case, values of y have been determined at successive points, $50\ \mu$ apart. The observations have been analysed taking a cell length, c , of $100\ \mu$, and the average value of $\bar{x}$ ($100\ \mu$) the average angular deviation between successive chords of length $100\ \mu$, is found to be 0.105° . The individual values of D obtained by the above procedure, are not independent, but the use of overlapping cells tends to reduce the effects of reading errors.

A similar analysis has been made using different values of c — $200\ \mu$, $300\ \mu$, etc. The mean values of $\bar{x}$ for different values of c are related by the equation $\bar{x}(c_1)/\bar{x}(c_2) = \sqrt{(c_1)}/\sqrt{(c_2)}$. The values of $\bar{x}(200\ \mu)$, $\bar{x}(300\ \mu)$, etc., can therefore be used to determine the value of $\bar{x}(100\ \mu)$ to which they are equivalent, and the corresponding values are included in Table I. It will be seen that $\bar{x}(100\ \mu)$ decreases with increasing cell size and reaches an approximately constant value. This is due to the fact that if the cell-length is too small, the apparent deviations in the track tend to be greater than the true values owing to reading errors, and the resulting value of $\bar{x}$ is too high. On the other hand, if the cell-size is unnecessarily large, the number of statistically independent observations is reduced, and the calculated values of $\bar{x}$ are subject to correspondingly greater

statistical fluctuations. It is therefore desirable to employ the smallest possible cell-size which is consistent with the condition that the uncertainty in the value of $\bar{x}$ due to reading errors is small (Goldschmidt-Clermont *et al.* 1948).

TABLE I.

Characteristic results of the measurements of the deviations in the track of a particle of length 8 mm. Readings every 50μ on first mm. of track. Grain-density in track 19.2 grains/ 50μ . $c=100\mu$.

x mm.	y dev.	S $y_n - y_{n+2}$	D $S_n - S_{n+2}$	x mm.	y dev.	S $y_n - y_{n+2}$	D $S_n - S_{n+2}$
12.8	5.6	0.5	0.3	12.25	7.0	0.4	0.3
12.75	5.7	0.6	0.6	12.2	7.3	0.2	0.2
12.7	6.1	0.2	0.1	12.15	7.4	0.1	0.1
12.65	6.3	0.0	-0.2	12.1	7.5	0.0	-0.3
12.6	6.3	0.1	0.0	12.05	7.5	0.0	-0.3
12.55	6.3	0.2	0.1	12.0	7.5	0.3	0.3
12.5	6.4	0.1	-0.2	11.95	7.5	0.3	0.3
12.45	6.5	0.1	-0.3	11.9	7.8	0.0	-0.1
12.4	6.5	0.3	-0.2	11.85	7.8	0.0	-0.1
12.35	6.6	0.4	0.0	11.8	7.8	0.1	0.0
12.3	6.8	0.5	0.3				

Values of $\bar{\alpha}(100\mu)$ for different values of c .

c microns	$\bar{D}$	$\bar{\alpha}(100\mu)^\circ$
50	0.141	0.191
100	0.22	0.105
150	0.285	0.074
200	0.35	0.060
300	0.54	0.050
400	0.78	0.047
600	1.56	0.051
1000	3.74	0.057
1400	6.28	0.058
2000	11.0	0.058

For small values of c , it is found that, owing to reading errors, values of $\bar{D}$ tend to become constant, and independent of c . It will be convenient to follow previous authors and refer to this as the "noise-level" ($\bar{D}_n$). The actual values of $\bar{D}_n$ depend on a number of factors such as the grain-density in the track, the quality and adjustment of the optical system of the microscope, and the individual skill of the observer, but they are of the order of 0.2μ .

As the cell-size, c , is increased from these low levels, the value of $(\bar{D})$ rises above the noise level $(\bar{D}_n)$. The corresponding values of $\bar{\alpha}(100\mu)$ then rapidly approach a constant value apart from statistical fluctuations. These effects may be summarized by saying that the errors of measurement become unimportant if $\bar{D} > 4\bar{D}_n$. The minimum value of c which gives this condition is adopted in the determination of $\bar{\alpha}(100\mu)$. It is clear that if the value of $\bar{\alpha}$ is to have a given statistical weight, the minimum length of track accepted for measurement will depend on the value of $\bar{\alpha}(100\mu)$, long tracks being necessary for particles of great energy. Thus if L is the length of the track, the number of statistically independent values of D is $(L/c) - 1$. It can be shown that the root-mean-square of the deviations of the individual values of D , from the true mean value corresponding to the momentum of the particle, is equal to $\sim 0.5D$. Approximate values of the minimum length of track required to ensure that the probable error in the determination of $\bar{D}$ is less than 25 per cent, are included, for different values of $\bar{\alpha}(100\mu)$, in Table II.

TABLE II.

Values of the minimum length of a track which allows the scattering parameter, $\alpha(100\mu)$, to be determined with a probable error of less than 25 per cent, in the absence of distortion.

Length of track mm.	$\alpha(100\mu)$ degrees
3	0.017
5	0.008
10	0.003
20	0.001

EFFECTS OF DISTORTION OF THE EMULSION.

When an exposed plate is processed, there is a large increase in the volume of the emulsion. If there is good adhesion between the gelatine and the glass, the swelling in the central regions of the plate corresponds approximately to a uniform linear transformation in the Z co-ordinates for any point; in the direction, that is, perpendicular to the glass. After fixation and washing, the drying of the plate produces the well-known shrinkage associated with loss of water and the removal of the silver salt from the emulsion during fixation. Since we are concerned only with deviations in the plane projection of a track, such a shrinkage will not, in principle, affect the measurements. In practice, however—and especially with thick emulsions, and in regions near the edges of the plate—some distortion of the emulsion occurs, so that a strictly rectilinear track will, in general, appear to be curved.

The distortion of the emulsion appears to arise, at least, in part, as a result of stresses released during the absorption of water, and because the top surface and sides are unconstrained. An emulsion, of which the cross-section in a plane perpendicular to the glass is rectangular when the

emulsion is dry, becomes distorted, therefore, when placed in the processing solutions. Further, the distortion may persist or be increased when the plate is dried. The difficulties can be greatly reduced by using large plates and confining the observations to the central areas; but even with these precautions, deviations due to distortion can give rise to serious errors in the determination of the energy of the fastest particles. ($\bar{\alpha}(100\mu) < 0.01^\circ$ per 100μ). In the worst cases, corrections may be necessary with tracks for which the true value of $\bar{\alpha}(100\mu)$ is as great as 0.05° .

Evidence for the existence of distortion can be obtained in two ways: first, it is sometimes found that the deviations, D , instead of being approximately equally distributed between positive and negative values, are all of one sign. In such cases, an inspection of more steeply dipping tracks, of which the projection is approximately parallel to that of the track under examination, can show whether distortion is indeed present.

Observations show that the distortion is commonly of such a character that the deviation which it produces in a strictly rectilinear track can be written as $\Delta = F\delta z$, (1), where Δ is the change in direction in the track in passing from a depth z to $z + \delta z$ in the emulsion, and F is a constant for a particular direction of the projection of the track in a given region of the plate. From observations on a more steeply dipping track, the constant F can be determined and appropriate corrections then made to the track under examination. If these corrections change the values of the deviations attributed to scattering so that they are now (apart from differences associated with statistical fluctuations) symmetrically distributed about the value zero, the corrected values are accepted as adequate for the determination of the true value of $\bar{D}$.

A better method, and the one most commonly adopted, is the following: distortion of the type represented by equation (1) has the result that the apparent deviations in the track are due to the joint effect of the deviations due to scattering, D , and those due to distortion, ϕ . The apparent deviations, D_a , may therefore be written as $D_a = D + \phi$, where ϕ is a constant term*. If the distortion is severe, so that ϕ is large, the values of D_a will be all of one sign in spite of the fact that values of D are equally positive and negative apart from statistical fluctuations.

An approximate value of ϕ may be obtained from the quantity $\Sigma D_a/n \sim \phi$, where ΣD_a represents the algebraic sum of the individual values of D_a . With this value of ϕ , the individual values of D can be found and hence an approximate value of $|\bar{D}|$. The value of $|\bar{D}|$ thus obtained is insensitive to the actual value of ϕ employed provided the error in ϕ is less than $|\bar{D}|/2$.

Table III. shows the results of measurements on a track which shows evidence of severe distortion. In addition to the correction ϕ calculated by the method described above, a number of arbitrarily chosen values

* It is a sufficient approximation to assume that the track "dips" at a constant inclination to the plane of the emulsion.

have been employed, and the results summarized in Table III. illustrate the fact that the final result is insensitive to the precise magnitude of the correction term.

TABLE III.

Observation on track showing evidence of distortion.

x mm.	y divs.	S $y_n - y_{n+2}$	D $S_n - S_{n+2}$	D* $\phi=4$ (D- ϕ)
9.1	10.0	-0.5	5.0	1.0
8.9	9.5	1.0	7.0	3.0
8.7	9.5	4.5	6.0	2.0
8.5	10.5	8.0	4.5	0.5
8.3	14.0	10.25	5.0	1.0
8.1	18.5	12.5	5.25	1.25
7.9	24.25	15.25	4.0	0.0
7.7	31.0	17.75	2.0	-2.0
7.5	39.5	19.25	1.25	-2.75
7.3	48.75	19.25	2.75	-1.25
7.1	58.75	20.5	3.25	-0.75
6.9	68.5	22.5	2.0	-2.0
6.7	79.25	23.75		
6.5	91.0	24.5		
6.3	103.0			
6.1	115.5			

$$\phi = \Sigma D/n = 4; \quad \Sigma D^*/n = 1.46$$

Values of $\alpha^*(100\mu)$ for different values of ϕ .

ϕ	$\Sigma(D-\phi)$	$\alpha^*(100\mu)$
0	48.0	0.12
1	36.0	0.09
2	25.5	0.064
3	20.0	0.050
4	17.5	0.044
5	18.5	0.046
6	26.0	0.065
7	36.0	0.090
8	48.0	0.12

LIMITATIONS OF THE METHOD.

The minimum value of $\bar{D}$ which can be regarded as significant, and therefore the maximum value of the energy of a particle which can be measured, depends on the length of the track available for measurement, the magnitude of the "noise-level", and the degree of distortion of the gelatine. The maximum measurable values of the energy corresponding to tracks of different length given in Table II., correspond to conditions in which distortion is absent. The minimum value of $\bar{\alpha}(100\mu)$ actually

observed in the present experiment is 0.001° , and we have no evidence to show whether the theoretical figure of $\bar{\alpha}(100\mu) = 0.0005^\circ$ for a track of length 2 cm., can in fact be attained in our experimental conditions. Such an observation, to be significant, would demand that the motion of the stage departs from being strictly rectilinear by an amount less than 0.4μ in traversing a distance of 2 cm. That a performance of this order of precision is obtained for shorter lengths of travel is proved by the observation of long tracks with a value of $\bar{\alpha}(100\mu) = 0.001^\circ$.

If distortion exists, then the minimum value of $\bar{D}$ which can be accepted as significant for a track of a given length is raised above the values given in Table II. By confining the observations to tracks in the central regions of the plates, however, and with the convention that the distortion correction ϕ is less than $2\bar{D}$, the number of tracks which are rejected when, but for distortion they would have given significant results, is very small.

CALIBRATION.

It has been shown (E. J. Williams 1939, 1940; Rossi and Greisen 1941) that if the track of a particle is divided into cells of length c , the average angular deviation between successive chords $\bar{\alpha}$, is related to the velocity v , of the particle by the equation

$$\bar{\alpha} = \frac{kZ}{m_0 v^2} (1 - \beta^2)^{\frac{1}{2}} \left\{ \left(\sqrt{\log \frac{\theta_{\max}}{\theta_{\min}}} \right) \right\}, \quad \dots \quad (2)$$

where Ze is the charge on the particle, and m_0 its rest-mass. The constant in equation (2) depends on the composition of the emulsion, and on the chosen length of cell, c . It is a sufficient approximation to neglect changes in the value of the logarithmic term in (2).

$$\bar{\alpha} = \frac{k_1 Z}{m_0 v^2} (1 - \beta^2)^{\frac{1}{2}} = k_2 \frac{Z}{pv}, \quad \dots \quad (3)$$

where m_0 is the rest-mass of the particle and p its momentum.

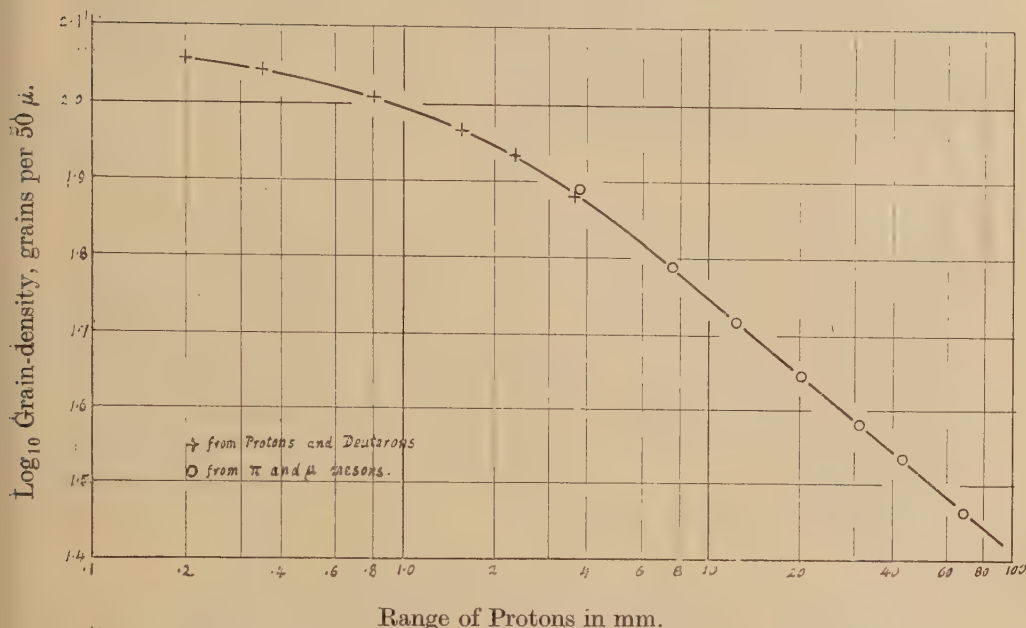
In order to determine the relation between the grain-density, g , in a track, and the rate of loss of energy of the particle producing it, observations have been made on the tracks of mesons, protons and deuterons of great range which stop in the emulsion. The results are shown in fig. 1. This curve, and the range-energy relation for the same particles, would allow us to determine the grain-density in the track of any particle of charge e , as a function of its velocity.

Direct determinations of the range-energy relation for protons in "electron-sensitive" emulsions have not yet been published. It is known, however, that in the Ilford G2 emulsions, the range R , in microns, of a proton with an energy E MeV., is given by the relation

$$R = CE^a$$

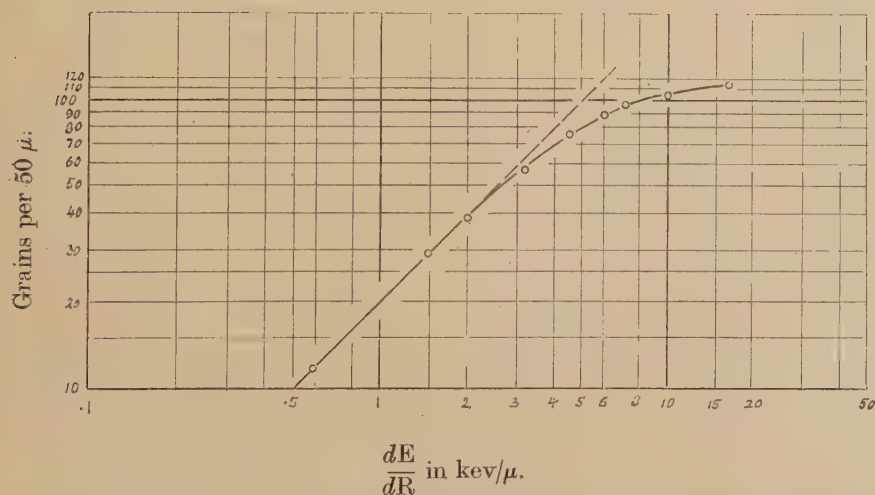
and that $dE/dR = kz^2\beta^n$ (4). Assume, therefore, that in the G5 emulsion a relationship of a similar type exists. The corresponding values of k and n can be determined from the following observations:

Fig. 1.



Grain-density in the track of a proton as a function of its residual range.

Fig. 2.



Relation between grain-density and rate of loss of energy along the trajectory.
Ilford G.5 emulsion.

(1) The average range in this emulsion of μ -mesons, emitted with a kinetic energy of 4.1 MeV. from a π -meson at rest, is $595 \pm 10 \mu$.

(2) From fig. 1, we determine the residual range of a proton which has an initial ionization, as determined from the grain density in its track, equal to that of energetic "primary" α -particles with a specific ionization equal to four times the minimum value for charge $|e|$.

From these two observations it is found that

$$\frac{dE}{dR} = \frac{0.587 Z^2}{\beta^{1.46}} \text{ KeV. per micron.} \quad . \quad . \quad (5)$$

This value of n is identical with that for the C2 emulsion.

Using this relation, together with the variation of the grain-density along the track of protons shown in fig. 1, we can determine the grain-density in the track as a function of the rate of loss of energy of the particle; see fig. 2. It will be seen that the relationship is almost linear for values of the rate of loss of energy up to four times the minimum value. From equation (5) and fig. 2, the relation between the grain-density in the track of an energetic proton, and the corresponding value of the scattering parameter $\bar{\alpha}$, can be determined.

EXPERIMENTAL RESULTS.

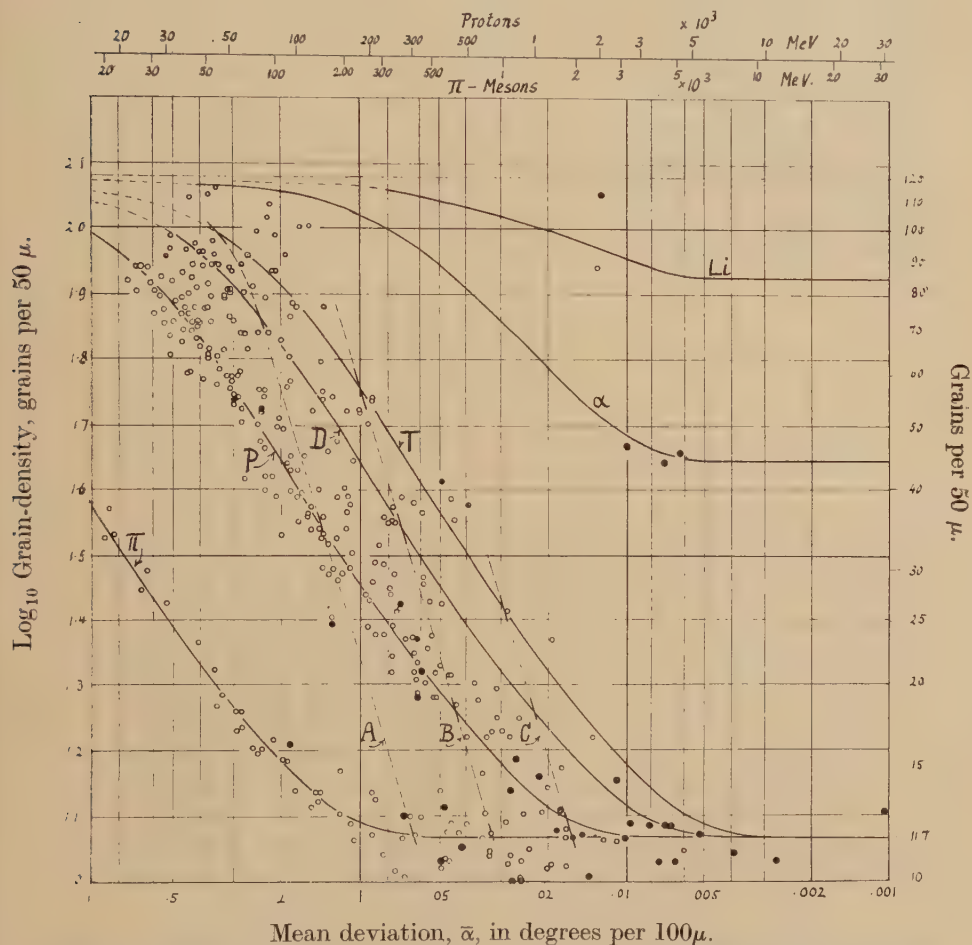
The methods employed in the previous paragraphs have been applied in a study of 350 tracks, associated with "stars", and chosen only because their length in the emulsion is greater than 3000μ . The observations were made in plates exposed at high altitudes as described in Part II. of the present series of papers. The results are represented in fig. 3 where the value of the scattering parameter, $\bar{\alpha}$, for a given track, is plotted against the corresponding value of the grain-density, g , both quantities being on a logarithmic scale.

The lines in fig. 3, marked π , P, D, and T are of the form to be expected for particles of charge e as determined by the methods of the preceding paragraphs. They are, however, displaced by about 7 per cent from the calculated curves for the corresponding particles along the axis of the scattering parameter. Their actual positions have been determined by the following method:

The calculated curve for protons has been displaced until it appears to give the best fit with the points corresponding to the most prominent group of particles. These are certainly due to protons. The other curves, with the same form as the first, are then drawn to correspond to particles of mass $286 m_p$, for π -mesons; and with appropriate values of the mass for deuterons and tritons. The corresponding curves for α -particles, lithium nuclei, etc. can also be deduced from the curve for protons using the information given in fig. 2. The difference of only 7 per cent between the calculated curve for protons and the observed distribution for these particles is not unexpected in view of the uncertainty in some of the quantities on which the calculations are based, but it remains to be explained.

In plotting the results shown in fig. 3, primary and secondary particles have been distinguished by the criteria described in (I.); (Brown *et al.* 1949). In the case of events in which many shower particles are emitted, a particle which produces a track with a direction near the axis of the cone

Fig. 3.



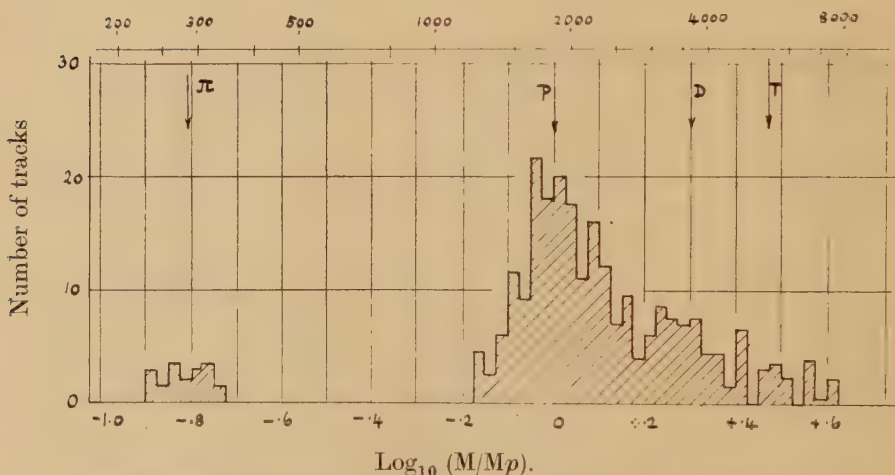
Relation between the grain-density and $\bar{\alpha}(100\mu)$, for the tracks of 350 particles.

"Primary" particles are shown thus ●; and "secondary" particles thus ○. The line P has the same form as the calculated curve for protons, but is displaced to the left, in the direction of the $\bar{\alpha}$ axis, by 7 per cent. The lines " π ", "D" and "T" are drawn in the correct relation to line P to correspond to particles of mass $286 m_e$, $3674 m_e$ and $5511 m_e$. "A", "B" and "C" are lines of constant momentum, and correspond to 500, 1000 and 2000 MeV./c, respectively. Energy scales, in MeV., for π -particles and protons are included at the top of the figure. It will be seen that the α -particles of great energy are all "primaries". The two points corresponding to particles of greater mass are due to a "primary" nitrogen and the "secondary" lithium nucleus occurring in the same event.

embracing the secondary particles, but on the opposite side of the star from the "shower" particles, is regarded as the primary. In the case of events of lower multiplicity, and especially in observations at great altitudes where the directions of motion of the primary particles are more widely dispersed than at 11,000 feet, the identification is subject to some uncertainty, and must be treated with reserve. The greater values of the energy of the primary, as compared with the secondary particles (see fig. 3) strongly suggests, however, that the errors in identification are not serious.

It will be seen, from an inspection of fig. 3, that the primary α -particles produce disintegrations with a frequency of the same order or magnitude as the protons in the same range of energies. On the other hand, compared with protons and deuterons, α -particles of great energy are emitted from nuclear disintegrations very infrequently.

Fig. 4.

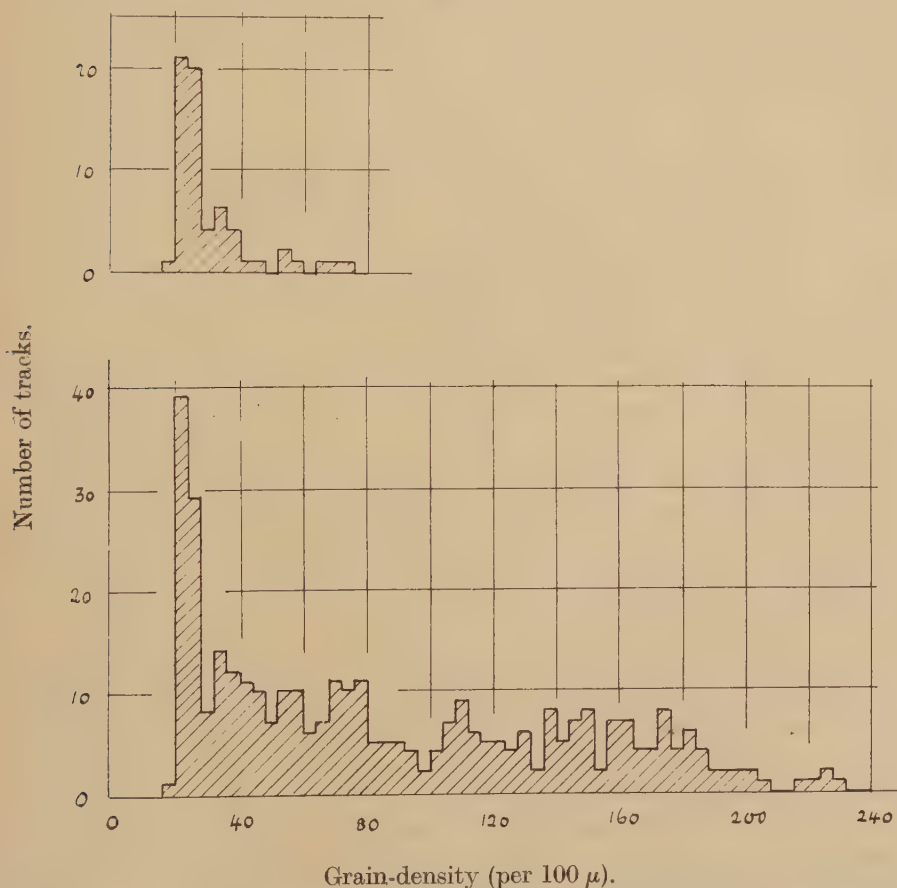
Mass in m_e .

Distribution in mass of the particles of charge $|e|$, corresponding to the measurements represented in fig. 3.

The displacement from the proton curve, in a direction parallel to the $\bar{x}$ -axis, of any observed point in fig. 3 gives a measure of the mass of the corresponding particle. The distribution in the values thus obtained—based on measurements of all the tracks represented in fig. 3 which have values of the grain-density lying in the interval from 15 to 98 grains per 50μ —is shown in fig. 4. It will be seen that in addition to the prominent peak due to protons, there are groups of smaller intensity, unresolved from the protons, which may be attributed to deuterons and tritons; and in addition, a well-defined group due to mesons of which the mean mass is $283 \pm 14 m_e$.

It may be emphasized that if, as an alternative procedure, the displacement of the individual points from the theoretical curve for protons had been measured, the resulting distribution in the values of the mass of the particles would have been identical in form with that shown in fig. 4, but all the values would have been lowered by 7 per cent. It is reasonable, however, to deduce the mass of the mesons by a direct comparison with that of protons, and the result obtained is identical with that given above. The majority of the mesons may therefore be identified as π -particles

Fig. 5.



Distribution in the values of the grain-density of the tracks of particles of charge $|e|$. The lower distribution is for all particles; and the upper, for those which are identified as π -mesons.

The observed distribution in the values of the grain-density of all the tracks of particles of charge e represented in fig. 3 is shown in fig. 5. This curve may be compared with the results of similar measurements made on

plates exposed on Jungfrauoch and given in (I.), fig. 1. The two distributions are similar in form, but there are relatively more particles of low grain-density in the present observations. This corresponds to the greater average energy of the nuclear explosions at the greater altitude, see (II.).

A study of fig. 3 shows that most of the particles producing tracks with a grain-density less than 14 grains per $50\ \mu$ are either mesons or "primary" particles. The nature of the secondary particles for which $\bar{\alpha}(100\ \mu) < 0.02^\circ$ cannot be determined by our present methods. It is possible, however, to extrapolate the observed distributions in energy of protons and π -mesons, in the range in which they can be distinguished, to the high energy region, and thus to estimate the proportion of the two types. Making suitable corrections for the "escape" of particles from the emulsion, the relative frequency of occurrence of the different types can be estimated, and the results are shown in Table IV.

TABLE IV.

Number of particles of different types, per "star", with a range greater than 3 mm., observed at an altitude of 70,000 feet.

π -particles	0.6,	Protons	1.4,
Deuterons	0.5,	Tritons	0.2,
α -particles	0.02.		

Average number of tracks per "star" = 7.4.

CONCLUSIONS.

The following conclusions can be drawn from the results of the present experiments :

(1) Of the mesons emerging with a kinetic energy less than 150 MeV. from nuclear disintegrations produced by protons and α -particles of great energy, the great majority are π -particles. If μ -particles are sometimes directly created, they are present in numbers less than 2 per cent of the π -particles.

(2) If electrons, or other charged particles of small rest-mass, are sometimes emitted from nuclear explosions, with an energy less than 150 MeV., they occur with a frequency less than 2 per cent of the π -particles. Most of the electrons of the soft component of the cosmic radiation have an energy less than 200 MeV. The observations therefore prove that most of them are of secondary origin.

(3) The observations give no support for the view that mesons of intermediate mass, τ -mesons with a lifetime greater than 10^{-12} sec., are ejected with an energy less than ~ 300 MeV., during nuclear explosions ; and they prove that if such particles, with a mass between 350 and $1200\ m_e$, are sometimes created in these processes, their number is less than 2 per cent of that of the π -mesons and less than 1 per cent of the protons. This conclusion is complementary to that drawn recently by Franzinetti (1950) from determinations by magnetic deflection experiments of the mass of slow charged particles produced by cosmic radiation.

(4) No final conclusion can be drawn regarding the nature of the particles, less massive than the proton, which produce tracks with the minimum value of the grain-density. In view of the observations on particles of lower energy, it is reasonable to suppose that the faster particles are of the same type. In what follows they will therefore be regarded as π -particles.

(5) At least 90 per cent of the "shower" particles emerging from nuclear explosions are π -mesons, a "shower" particle being defined as one with a grain-density less than $1.5 g_{\min}$ (see I.). Consider, however, all particles in a given range of momentum—say between 200 and 700 MeV./c—a practice commonly adopted in experiments with Wilson chambers operated in magnetic fields. Among the particles in this momentum range, the π -mesons are accompanied by large numbers of protons. If the π -mesons are equally distributed between positive and negative particles, the "positive excess" should be of the order of six, a value consistent with that observed in experiments with expansion chambers. (Rochester 1949).

(6) An extension of the observations will allow a detailed analysis of the nuclear processes produced by protons and α -particles in the range of energies above 10^9 eV., including the distribution in energy of the π -mesons near their points of production, and the relation between the energy of a π -particle and its direction of emission with respect to the "primary" particle. Such investigations are being undertaken in a collaboration with U. Camerini, W. O. Lock and H. Muirhead; and by J. H. Davies and C. Franzinetti.

(7) The observed homogeneity in the values of the mass of the ejected mesons with energy less than 150 MeV. allows us to exclude certain assumptions regarding the origin of the particles. It is known, from the experiments on the artificial creation of π -mesons made at Berkeley (Gardner and Lattes 1949), that the threshold for the process occurs at such an energy of the bombarding protons or α -particles that the creation of a particle of mass $\sim 280 m_e$ is just possible from the point of view of the conservation laws. It follows that the π -mesons must be directly created: that they cannot be regarded as the products of decay of mesons of appreciably greater mass, and very short lifetime.

In the nuclear transmutations with which we are concerned, limitations of energy do not apply. In principle, therefore, the possibility cannot be excluded that the π -mesons occurring in showers are produced by the decay of short-lived mesons of greater mass which are the primary products of the nucleon-nucleon collisions. The observed homogeneity in the values of the mass of the ejected mesons proves, however, that any postulated unstable parent of the π -particles, if it exists, must be very short-lived: for if it survived, on the average, over a length of path of say 2 mm., the observed values of the mass would represent averages between the masses of the parent and daughter particles. As a result, we should expect to observe a dispersed set of values instead of the compact

group actually found. The present observations therefore prove that any more massive parent mesons have lifetimes less than 10^{-13} sec. It is, of course, reasonable to suppose that the π -mesons are directly produced in the nucleon-nucleon collisions.

ACKNOWLEDGMENTS.

In conclusion, the author wishes to record his sincere thanks to Professor C. F. Powell for his encouragement and help; to Dr. H. Heitler and Mr. J. Webb for their assistance; to Messrs. W. O. Lock and H. Muirhead for processing the Ilford G. 5 plates, with emulsions 400μ thick, employed in the investigation; and to the team of observers in this Laboratory who scanned the plates.

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XVI. *The S-Matrix for Meson-Nucleon Interactions.*

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ABSTRACT.

The possibility is considered of obtaining a divergence free S-matrix for the interactions of mesons with nucleons along the lines of mass and charge renormalization, which Dyson has so successfully applied to quantum electrodynamics. It has been shown that this can be done for the vector interaction of neutral vector mesons. The procedure is here extended to the scalar interactions of scalar and pseudo-scalar mesons but proves to be quite inadequate to remove all the divergences in the other cases.

§ 1. INTRODUCTION.

By applying Feynman's (1949 a, b) graphical methods for the calculation of matrix elements to relativistic quantum electrodynamics in the Schwinger (1948) form, Dyson (1949 a, b)† has shown how a finite S-matrix can be obtained for a wide class of phenomena. In Feynman's theory, any real process taking place with specific virtual processes can be represented by a graph from which the integral for the corresponding matrix element can be written down directly, each line and each vertex corresponding to a single factor in the integrand. An essential feature of Dyson's development is the proof that only a limited number of different types of divergence can occur in quantum electrodynamics. These are called primitive divergents. When a primitive divergent graph occurs as part of a larger graph its effect is to complicate a single line or a single vertex of a simpler graph, and consequently to modify a single factor of the integrand corresponding to the simpler graph. If the infinite parts of all such modifications of a graph are dropped in a well-defined way, a finite S-matrix is obtained for all phenomena which do not involve bound states. The mass and charge of a free particle in the vacuum are both given by the theory as infinite renormalizations of the mass and charge of an ideal 'bare' particle. Dyson has shown that his prescription for dropping the infinite terms is equivalent to equating the infinite theoretical values of mass and charge to the finite experimental values.

The extension of this method to the various meson-nucleon interactions is here considered. The number and degree of the possible primitive divergents in any theory are closely related to the degree of the derivatives

* Communicated by Dr. N. Kemmer.

† These papers will be referred to as I. and II.

of Δ -functions which occur in the commutation relations of the Hamiltonian under consideration. The meson interactions which in this respect most closely resemble electrodynamics are the scalar interactions of scalar and pseudo-scalar mesons with nucleons in which no derivatives occur from meson variables. The possible types of primitive divergents are here identical with those of electrodynamics. In electrodynamics one of these—the scattering of light by light—is finite by gauge invariance, but the scattering of mesons by mesons gives rise to genuine divergences. However, it will be shown that these can be regarded as a special type of self-energy between pairs of mesons and can be cancelled by adding the appropriate δ -type interaction between mesons to the Lagrangian. A finite S-matrix will thus be obtained. In the remaining meson-nucleon interactions double derivatives arise from the commutation relations of the meson variables with the result that there is no limit to the number and degree of the possible types of primitive divergents. Thus the renormalization of mass and charge is shown to be quite inadequate for the removal of all divergences in these cases. The only exception to this is the vector interaction of neutral vector mesons with nucleons, which has already been dealt with elsewhere (Matthews 1949 b).

The proofs of this paper do not confirm exactly the conclusions of Case (1949) which were generalizations from the results of particular calculations. Some of the infinities considered here only occur in comparatively high-order corrections and were thus not detected.

§ 2. THE S-MATRIX.

The interaction of two fields can be expressed by a generalized Schrödinger equation in the interaction representation,

$$i\hbar\delta\Psi[\sigma]/\delta\sigma(x)=H(\phi(x))\Psi[\sigma], \quad (1)$$

where $\Psi[\sigma]$ is the wave function on a general space-like surface, σ , and $\phi(x)$ is a typical field variable satisfying the equation of motion and the commutation relations of its free field with mechanical mass. The Hamiltonian in (1) has matrix elements for transitions which cannot occur with conservation of energy and momentum, and it is convenient to remove these by a Schwinger (1948) transformation

$$\Psi \rightarrow \exp\{-iS(\phi)\}\Psi. \quad (2)$$

The new equation is

$$i\hbar(\delta/\delta\sigma)(\exp\{-iS(\phi)\}\Psi)=H(\phi)\exp\{-iS(\phi)\}\Psi. \quad (3)$$

To second order in the coupling constant the new Hamiltonian has matrix elements for real processes and also some infinite elements for the self-energies of the interacting particles. If the infinite self-energy parts of the Hamiltonian in (3) are $H_e(\phi)$, it has been shown for a fermion field ψ and a boson field ϕ_μ , (Matthews 1949 c), that

$$H_e(\phi, \psi)=\hbar c\delta\kappa_0\bar{\psi}\psi+\frac{1}{2}\delta\kappa^2\phi_\mu, \quad (4)$$

where κ_0 and κ are the reciprocal Compton wavelengths for the fermions and the bosons respectively. To obtain an equation from which these terms have been removed make the transformation

$$\Psi = U \Psi_e, \quad (5)$$

where

$$i\hbar c \delta U / \delta \sigma = H_e(\phi) U. \quad (6)$$

It then follows that

$$i\hbar c U^{-1} \delta U / \delta \sigma = H_e(\phi_e), \quad (7)$$

where

$$\phi_e = U^{-1} \phi U. \quad (8)$$

The equation which Dyson makes the starting-point of his theory is obtained by reversing the order of these transformations. The transformation (5) on equation (1) leads to

$$i\hbar c (\delta \Psi_e / \delta \sigma) + i\hbar c U^{-1} (\delta U / \delta \sigma) \Psi_e = H(\phi_e) \Psi_e.$$

By (7),

$$\begin{aligned} i\hbar c \delta \Psi_e / \delta \sigma &= \{H(\phi_e) - H_e(\phi_e)\} \Psi_e \\ &= H_1(\phi_e) \Psi_e, \end{aligned} \quad (9)$$

which is the Schrödinger equation in the interaction representation in a form which is free from self-energy effects up to the second order in the coupling constant. Since ϕ satisfies the free field equation with mechanical mass, it follows from (4), (6) and (8) that ϕ_e satisfies the free field equation with renormalized mass. This is given infinite by the theory, but since it is the mass of the observed free particle, it is equated to the finite experimental mass. An equation like (3) with the self-energy explicitly subtracted could now be obtained from (9) by performing the transformation (2) with ϕ replaced by ϕ_e .

Dyson's theory starts with an equation of the form (9), but the constants $\delta\kappa_0$ and $\delta\kappa^2$ are chosen as power series in the coupling constant so that they will cancel all the self-energy effects from the rest of the Hamiltonian up to any order. If Ψ_0 is the state vector of a system on a surface in the remote past and Ψ is the same system, after its particles have interacted, in the distant future, then

$$\Psi = S(\infty) \Psi_0, \quad (10)$$

where in Dyson's notation (I. § 5; II. § 2)

$$S(\infty) = \sum_{n=0}^{\infty} \left(\frac{-i}{\hbar c} \right)^n \frac{1}{n!} \int_{-\infty}^{\infty} dx_1 \dots \int_{-\infty}^{\infty} dx_n P(H_1(x_1), H_1(x_2), \dots, H_1(x_n)). \quad (11)$$

$S(\infty)$ is the Heisenberg S -matrix, and, by developing Feynman's (1949 a, b) methods, Dyson has given comparatively simple rules for the calculation of its elements (I. §§ 6, 7; II. § 2). Essentially, if H_1 contains factors ψ , $\bar{\psi}$ and ϕ , where

$$[\phi(x), \phi(y)] = i\hbar c \Delta(x-y), \quad (12)$$

and

$$\{\psi(x), \bar{\psi}(y)\} = -i(\gamma_\mu \partial / \partial x_\mu - \kappa_0) \Delta(x-y), \quad (13)$$

the matrix element for a process in which a virtual particle passes between x and y , contains in the integrand a factor

$$\langle P(\phi(x), \phi(y)) \rangle_0 = \frac{1}{2} \hbar c \Delta_F(x-y) \quad . \quad . \quad . \quad (14)$$

if the particle is a boson, and

$$\langle P(\bar{\psi}(x), \psi(y)) \rangle_0 = -\frac{1}{2} \eta(x, y) (\gamma_\mu \partial / \partial x_\mu + \kappa_0) \Delta_F(x-y) = -\frac{1}{2} \eta(x, y) S_F(x-y)$$

if it is a fermion. If, in place of ϕ , H_1 contains a factor $\partial \phi / \partial x_\mu$, then it will also contain a term depending explicitly on the normal to the surface σ . It has already been shown (Matthews 1949 a) that to extend Dyson's rules to this case the normal-dependent terms in H_1 can be neglected and then effectively

$$\langle P(\partial \phi / \partial x_\mu, \partial \phi / \partial y_\nu) \rangle_0 = \frac{1}{2} \hbar c (\partial^2 / \partial x_\mu \partial y_\nu) \Delta_F(x-y). \quad . \quad . \quad (15)$$

A similar result holds if the derivatives occur in the commutation relations themselves. Thus for vector mesons

$$[\phi_\mu(x), \phi_\nu(y)] = i \hbar c (\delta_{\mu\nu} + (1/\kappa^2) \partial^2 / \partial x_\mu \partial y_\nu) \Delta(x-y), \quad . \quad . \quad (16)$$

and to calculate terms of (11) for a Hamiltonian containing a factor ϕ_μ , the normal-dependent terms can be neglected and effectively

$$\langle P(\phi_\mu(x), \phi_\nu(y)) \rangle_0 = \frac{1}{2} \hbar c (\delta_{\mu\nu} + (1/\kappa^2) \partial^2 / \partial x_\mu \partial y_\nu) \Delta_F(x-y). \quad . \quad (17)$$

The infinities in $S(\infty)$ associated with mass renormalizations have already, in principle, been removed. There remain other infinities which in electrodynamics can be removed entirely by renormalization of the charge. Before considering the possible application of this method to meson interactions, it will be necessary to discuss in more detail Dyson's analysis of the possible types of primitive divergents, because it is at this point that the difficulties of extending the theory arise.

§ 3. PRIMITIVE DIVERGENTS.

Consider an interaction between fermions and bosons in which no derivatives occur either in the interaction or in the commutation relations of the bosons. Every element of $S(\infty)$ is associated with certain graphs G , the process under consideration determining the number of external fermion lines, E_f , and the number of external boson lines, E_b . Consider any such graph, G , with n vertices and F internal lines of which F_f are fermion lines and F_b are boson lines. Now

$$\Delta_F(x) = \frac{-i}{(2\pi)^3} \int \frac{\exp\{-ip_\mu x_\mu\}}{p_\mu^2 + \kappa^2} d^4 p_\mu. \quad . \quad . \quad (18)$$

The integrals over the space variables in the elements of $S(\infty)$ are trivial, giving conservation of energy and momentum at each vertex. Thus the energy-momentum associated with each line in G can be expressed in terms of $(F-n+1)$ basic vectors p^i , and the corresponding contribution to $S(\infty)$ is an integral, M , over these variables. For considerations of

convergence, each boson line contributes to the integrand of M a factor $1/((\Sigma a_i p^i)^2 + \kappa^2)$ and each fermion line a factor $\Sigma a_i p_\mu^i / ((\Sigma a_i p^i)^2 + \kappa_0^2)$, where $\Sigma a_i p^i$ is the energy-momentum associated with the line. The numerator of the fermion factor comes from the derivative of the Δ -function in the fermion commutation relation (13). Many of the coefficients a_i will be zero and, if for a certain line only a_i is non-zero, the line will be referred to as a basic line. If an internal line in a graph is replaced by two external lines, the line is said to be opened.

The differentials $d^4 p_\mu$ can be expressed in polar variables. The integrals over the angle variables are finite and the integral over the radius is $p^3 dp$. Define the convergence function

$$K = 2F - F_f - 4(F - n + 1). \quad (19)$$

If there is only one basic p^i , $-(K + 1)$ is the power of p in the integrand of M expressed in polar variables. The condition for convergence is in this case

$$K \geq 1. \quad (20)$$

If there are several basic variables, define K_i to be K evaluated for the graph obtained by opening all the basic lines except p^i , that is for the integral M with all variables except p^i held constant. Similarly define K_{ij} to be K evaluated for the graph with all basic lines except p^i and p^j opened. A sufficient condition for M to be conditionally convergent is that

$$K_i \geq 1, \quad K_{ij} \geq 1, \dots, K \geq 1, \quad (21)$$

for all $i, j, \dots = 1, 2, \dots, (F - n + 1)$. The graph is absolutely convergent if (21) holds for all possible choices of the basic variables p^i . This condition is not necessary for convergence because it may happen that the coefficients of the higher powers of p in M vanish identically.

A graph is said to be primitive if the graphs obtained from it by opening any line are convergent. Thus a primitive graph certainly satisfies all the conditions (21) except possibly the last one. If this is also satisfied, the graph is itself convergent. The only possible primitive divergent graphs are those for which the last condition is not satisfied. That is if

$$K > 1. \quad (22)$$

If G has n_f vertices with just two fermion lines incident, and n_b vertices with just two boson lines incident, then

$$2F = 3n - n_f - n_b - E_f - E_b, \quad (23)$$

and

$$F_f = n - n_b - \frac{1}{2}E_f. \quad (24)$$

Thus

$$K = (3/2)E_f + E_b + n_f + 2n_b - 4, \quad (25)$$

and the only possible primitive divergents are (i) $E_f = 2, E_b = 0$; (ii) $E_f = 2, E_b = 1$; (iii) $E_f = 0, E_b = 2$; (iv) $E_f = 0, E_b = 4$, and two other graphs which contain odd fermion loops which cancel with the similar graphs obtained

by reversing the directions of the lines in the loop. The graphs (i), (ii) and (iii) are self-energy and vertex parts which can be regarded as modifications of single lines or single vertices. The graphs (iv) represent the scattering of bosons by bosons and will be called "square" parts. The simplest, containing four free boson and a loop of four fermion lines, will be called a simple square part, S_1 .

Now any divergent graph must be a divergent primitive or contain divergent primitive parts and a convergent graph can only be made divergent by the insertion of primitive divergent parts. Dyson showed, (II, § 6), by general arguments of gauge invariance that for electrodynamics no new infinities arise from the insertion of square parts. These arguments are of course not applicable to mesons, and by Dyson's methods it can be shown by direct calculation that the scattering of scalar or pseudo-scalar mesons by themselves is not finite like the scattering of light by light. Thus for meson interactions a special consideration of square parts is necessary.

For a single free meson in the vacuum the self-energy arises from the virtual creation of nucleon pairs. When there are two free mesons these can scatter each other by virtual nucleon pair creation, (square graph). The matrix element for this process is infinite, but a finite part can be separated off if, in the spirit of Dyson's work, we subtract from it that part which is obtained by setting the energy-momenta of the free mesons equal to zero. This subtracted part can be regarded as a special type of self-energy, which will have the form $\hbar c \delta \lambda \phi^4$, where $\delta \lambda$ is an infinite constant. In the next section, it will be shown how a finite S-matrix can be obtained up to any order for certain meson interactions by the addition of a term of this type to the Lagrangian for the interaction.

Note that the $\delta \lambda$ effect, unlike the $\delta \kappa^2$, is essentially an interaction between mesons which will not take place for a single free meson. The term is thus properly included in the interaction Lagrangian, when it will occur as an additional term in the Hamiltonian of (1) and, after the transformation (5), in the Hamiltonian $H_1(\phi_c)$ of (9). It would not be a reasonable procedure to start with the usual Lagrangian and to add the term to the self-energy Hamiltonian, H_c , of (4). It would then appear both in $H_1(\phi_c)$ of (9) and in the free field Hamiltonian determining the motion of ϕ_c . But the equation of motion of ϕ_c should be the wave equation for a single free meson which, as pointed out above, should not depend on $\delta \lambda$.

§ 4. SCALAR MESON SCALAR INTERACTIONS.

The only interactions, in addition to electrodynamics, which satisfy the condition at the beginning of the last section are the scalar interactions of scalar and pseudo-scalar mesons with nucleons. If the term $\hbar c \delta \lambda \phi^4$ is added to the Lagrangian in the pseudo-scalar case, the Hamiltonian $H_1(x)$ of (9) is

$$H_1(x) = i f \bar{\psi}(x) \gamma_5 \psi(x) \phi(x) - \hbar c \delta \kappa_0 \bar{\psi}(x) \psi(x) - \frac{1}{2} \delta \kappa^2 \phi^2(x) - \hbar c \delta \lambda \phi^4(x). \quad (26)$$

This Hamiltonian will give rise to graphs in which the most important vertices will have two nucleon and one meson line incident, at which the first term of (26) is operating. There will also be vertices at which either two nucleon, two meson or four meson lines are incident. At these vertices the terms $\delta\kappa_0$, $\delta\kappa$ and $\delta\lambda$ respectively will be operating. The rules for obtaining the matrix elements from the graphs are the same as those given by Dyson, (II. §§ 2, 3), with the following substitutions. $A_\mu(x)$ is replaced by $\phi(x)$, e is replaced by $-f$, γ_μ is replaced by γ_5 and $D_F(x)$ is replaced by $\Delta_F(x)$. Also if n_l is the number of vertices at which $\delta\lambda$ is operating, in place of II. Eq. (12), terms must be multiplied by

$$(-1)^{n-n_m-n_l-l-m} \dots \dots \dots (27)$$

This term makes allowance for the changes of sign which are due to the rearrangement of the ψ and $\bar{\psi}$ factors to bring associated pairs adjacent, (I. §§ 6, 7). As in electrodynamics, functions $\Sigma(W)$, $\Pi(W')$ and $\Lambda(V)$ can be defined, (II. Eqs. (27), (39), (32)) through which can be determined the alteration in the integrand due to the insertion of a nucleon self-energy part, W , a meson self-energy part, W' , or a vertex part, V . If W consists of a single vertex,

$$\Sigma(W, t^1) = -2\pi i \delta\kappa_0 \dots \dots \dots (28)$$

If W' is a single vertex,

$$\Pi(W', t^1) = \pi i \delta\kappa^2 \dots \dots \dots (29)$$

The different signs of the terms in (28) and (29) are due to the factor (27). It is also necessary to consider explicitly the integrals from square graphs, S , which will be of the form

$$\Delta_F(t^1)\Delta_F(t^2)\Delta_F(t^3)\Delta_F(t^1+t^2-t^3)K(S, t^1, t^2, t^3).$$

In general, $K(S)$ is itself a function of Δ_F , S_F and γ_5 . In the special case when S is a single vertex,

$$K(S, t^1, t^2, t^3) = i\delta\lambda \dots \dots \dots (30)$$

In Dyson's terminology, a "proper" vertex or self-energy part is one which cannot be split into two parts joined by a single line. An "irreducible" graph is one from which all self-energy and vertex parts have been removed. It is also convenient to consider irreducible self-energy and vertex parts, which are such parts that are proper and from which all internal self-energy and vertex parts have been removed. We now extend these definitions. A "quasi-proper" square part is a square part which cannot be split into a square part joined to a self-energy part by a single line. A "proper" square part is a quasi-proper square part which cannot be split into two square parts joined by two meson lines. "Totally irreducible" graphs are irreducible graphs which contain only simple square parts. $\Sigma(t^1)$ is the sum of $\Sigma(W, t^1)$ over all fermion self-energy parts, and $\Sigma^*(t^1)$ is the sum over all proper fermion self-energy parts. $\Pi(t^1)$ and $\Pi^*(t^1)$ are similarly defined. Square parts which are not quasi-proper are clearly redundant. Thus $K(t^1, t^2, t^3)$ is defined as the sum over all quasi-proper square parts and $K^*(t^1, t^2, t^3)$ as the sum over all proper square parts.

To obtain the matrix element for a given process, one must consider the totally irreducible graphs for the process. The corresponding integrals will be made up of factors S_F , Δ_F , γ_5 and $K(S_1)$ (from the simple square parts). To make allowance for the insertion of self-energy parts into the lines of such graphs, the factors S_F and Δ_F must be replaced by S'_F and Δ'_F , which are implicitly defined by the equations (II. Eqs. (63), (64)),

$$S'_F(t^1) = S_F(t^1) + S_F(t^1) \Sigma^*(t^1) S'_F(t^1), \quad . \quad . \quad . \quad (31)$$

$$\Delta'_F(t^1) = \Delta_F(t^1) + \Delta_F(t^1) \Pi^*(t^1) \Delta'_F(t^1). \quad . \quad . \quad . \quad (32)$$

These equations express the fact that a self-energy part is either proper or is a proper self-energy part attached by a single line to a self-energy part, which may be proper or improper. The insertion of all quasi-proper square parts in place of a simple square part is allowed for by replacing the factor $K(S_1)$ by K . Now a quasi-proper square part is either a proper square part or is a proper square part joined to a quasi-proper square part by two meson lines, which may themselves contain self-energy parts. Thus, corresponding to (31) and (32), K is implicitly defined by the equation

$$K(t^1, t^2, t^3) = K^*(t^1, t^2, t^3) + \int K^*(t^1, t^2, t) \Delta'_F(t) \Delta'_F(t^1 + t^2 - t) K(t, t^1 + t^2 - t, t^3) d^4t. \quad . \quad . \quad (33)$$

No infinity will arise from the integral over t . $\Delta(t^1, t^2)$ is summed over all proper vertex parts only, and the effect of inserting vertex parts into the totally irreducible graphs is allowed for by replacing γ_5 by $\Gamma(t^1, t^2)$, which is defined by

$$\Gamma(t^1, t^2) = \gamma_5 + \Delta(t^1, t^2). \quad . \quad . \quad . \quad (34)$$

All the infinities in the matrix elements will appear in the functions S'_F , Δ'_F , Γ and K . It must now be shown how these can be removed.

Consider for the moment only totally irreducible parts. If S is a totally irreducible square part, then $K(S, t^1, t^2, t^3)$ contains divergent factors $K(S_1)$ from the simple square parts contained in S . These simple square parts can each be replaced by a single vertex at which $\delta\lambda$ is operating, and the first term in the expansion of $\delta\lambda$ (of order f^4) can be chosen to cancel these infinities. (The higher-order terms in $\delta\lambda$ will be defined later to cancel certain other infinities which arise when irreducible square parts are considered.) With this understanding, the integral $K(S, t^1, t^2, t^3)$, as a whole, still diverges logarithmically. By splitting off the part obtained by setting $t^1 = t^2 = t^3 = 0$ and summing over all totally irreducible square parts,

$$K^*(t^1, t^2, t^3) = A'' + i\delta\lambda + K_c^*(t^1, t^2, t^3), \quad . \quad . \quad . \quad (35)$$

where A'' is an infinite constant and K_c^* is a uniquely defined finite function. With the same understanding about simple square parts, the logarithmically divergent $\Delta(V, t^1, t^2)$ can be split into a finite constant and a finite part. By summing over all totally irreducible vertex parts, V , we have

$$\Delta(t^1, t^2) = L\gamma_5 + \Delta_c(t^1, t^2). \quad . \quad . \quad . \quad (36)$$

Totally irreducible self-energy parts do not contain any square parts (see below), and can be split up as in electrodynamics (II. Eqs. (67), (77)),

$$\Sigma^*(t^1) = A - 2\pi i \delta \kappa_0 + B(t_\mu^1 \gamma_\mu - i \kappa_0) + (t_\mu^1 \gamma_\mu - i \kappa_0) S_c(t^1), \quad . \quad . \quad (37)$$

$$\Pi^*(t^1) = A' + \pi i \delta \kappa^2 + C((t^1)^2 + \kappa^2) + ((t^1)^2 + \kappa^2) \Delta_c(t^1). \quad . \quad . \quad (38)$$

L , A , B , A' and C are infinite constants and $\Delta_c(t^1)$, $S_c(t^1)$ and $A_c(t^1, t^2)$ are defined by absolutely convergent integrals. Substituting these expressions into (31), (32), (33) and (34), equations are obtained for $S'_F(t^1)$, $\Delta'_F(t^1)$, $K(t^1, t^2, t^3)$ and $\Gamma(t^1, t^2)$. S'_{F1} , Δ'_{F1} , Γ_1 and K_1 are defined to be the functions which are obtained if the infinite constants are simply dropped from these equations. Note that so far no account has been taken of self-energy, vertex and square parts which are not totally irreducible.

It will now be shown that, by successive approximation, it is possible to develop power series in the coupling constant for finite functions S'_{F1} , Δ'_{F1} , K_1 and Γ_1 even when graphs which are not totally irreducible are considered. Suppose that the series for these functions have been developed up to f^{2n} . To develop the next term of the series for K_c^* , consider the contribution from a totally irreducible square graph, S , of order l , ($l \leq 2n+4$). The integral corresponding to this graph will contain factors S_F , Δ_F and γ_5 and factors $K(S_i)$ for the simple square parts. The exact integral is obtained by replacing these by S'_{F1} , Δ'_{F1} , Γ_1 and K_1 respectively. These will not introduce any divergencies and will determine the integrand up to the order f^{2n+l} . The whole integral will itself diverge logarithmically, but the finite part can be separated from an infinite constant by the usual procedure to determine $K_c(S)$ and $A''(S)$ to the order f^{2n+l} . Since $l \geq 4$, by summing over all such graphs, S , power series in f can be developed for K_1 and A'' up to the order f^{2n+4} .

To obtain Γ_1 to order f^{2n+2} , sum in the same way over all totally irreducible vertex graphs, V , after substituting the corrected functions for the line, vertex and simple square factors. The logarithmically divergent integrals can again be split into an infinite constant and a convergent part to give power series for L and A_c up to f^{2n+2} . Hence Γ can be found to the same order and Γ_1 by dropping the infinite constant L .

To obtain similar expressions for S'_{F1} and Δ'_{F1} , it is not necessary to consider explicitly the inclusion of square parts; because the only irreducible self-energy parts are loops with two vertices, (II. Figure 5); and square parts can only be included as sub-parts of included vertex parts. They will thus be allowed for by the substitution of Γ_1 for γ_5 . The development of S'_{F1} and Δ'_{F1} will thus be just the same as in electrodynamics.

Since the infinite constant A'' can be developed as a power series in f , the constant $\delta\lambda$ can be chosen to satisfy

$$A''(f) + i\delta\lambda(f) = 0. \quad . \quad . \quad . \quad . \quad . \quad . \quad (39)$$

(This is consistent with the choice of the first term of $\delta\lambda$ made above.) Then no infinities will arise from square parts provided the sum is taken over all such parts at each stage: K^* is equal to K_c^* and K_1 is identical

with K . But such summations always are taken in the procedure laid down by Dyson. Thus, if this choice of $\delta\lambda$ is made, no infinities will arise from square parts if Dyson's procedure for electrodynamics is followed for this interaction. In particular Dyson's proof (II. § 7), that the dropping of the other infinite constants is equivalent to a 'charge' renormalization,

$$f_1 = Z_1^{-1} Z_2 Z_3 f \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (40)$$

can be taken over directly, with the trivial addition that $\delta\kappa^2$ must be chosen to satisfy

$$\delta\kappa^2 = (-1/\pi i) Z_3^{-1} A'(f_1). \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (41)$$

The renormalized 'charge' f_1 can be equated to the finite experimental value and a finite S-matrix is thus obtained for effects arising from this interaction. Strictly speaking the elements of the S-matrix have been derived as a power series in f with finite terms. The convergence of the series itself has not been discussed.

Exactly the same argument applies to the scalar interaction of scalar mesons with nucleons if γ_5 in the above is replaced by $-i\delta_{\alpha\beta}$, where $\delta_{\alpha\beta}$ is a Kronecker δ -symbol operating on the spinor suffixes of ψ and $\bar{\psi}$.

§ 5. OTHER MESON-NUCLEON INTERACTIONS.

In all the remaining meson-nucleon interactions the condition of § 3 is not satisfied, and the factor corresponding to a meson line in an integral M will contain a double derivative of a Δ_F -function. Thus, for considerations of convergence, a meson line will contribute to M a factor

$$(\Sigma a_i p_\mu^i)(\Sigma a_i p_\nu^i)/((\Sigma a_i p^i)^2 + \kappa^2).$$

The new convergence function K^D is defined

$$K^D = F_f - 4(F - n + 1). \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (42)$$

This function has the same properties with regard to the convergence of the integrals now under consideration as K had for the interactions previously considered. The expressions (23) and (24) for F_f and F are still valid so that

$$K^D = (3/2)E_f + 2E_b - n + n_b + n_f - 4. \quad . \quad . \quad . \quad . \quad . \quad . \quad (43)$$

A primitive graph certainly converges if

$$K^D \geq 1, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (44)$$

but primitive graphs will be primitive derivatives if, by (43),

$$(3/2)E_f + 2E_b < n + 5. \quad . \quad . \quad . \quad . \quad . \quad . \quad (45)$$

Owing to the appearance of n on the right-hand side of this inequality, there is no restriction on the number and degree of the primitive divergents. An irreducible divergent graph may be found for any real process provided sufficient virtual processes are included. The integrals will only converge if the coefficients of all the divergent powers of the basic energy-momenta vanish identically. That this is not always so can be proved by any particular example. Thus for these interactions the renormalization of mass and charge is quite inadequate to remove all the divergences.

The only exception to this is in the vector interaction of neutral vector mesons, in which the derivatives in the factor (17) come from the commutation relations themselves (16) and not from derivatives of the commutation relations as in (15). If the Stückelberg (1938) form is used, in which two subsidiary fields are introduced, it can be seen that the derivatives arise from a vector interaction of the subsidiary scalar field. This can be eliminated by a transformation, and Dyson's treatment of electrodynamics can then be applied without the necessity of introducing a $\delta\lambda$ term. This interaction has already been dealt with elsewhere (Matthews 1949 b), where it is shown that (17) can be replaced by

$$\langle P(\phi_\mu(x), \phi_\nu(y)) \rangle_0 = \frac{1}{2} \hbar c \delta_{\mu\nu} \Delta_F(x-y). \quad (46)$$

§ 6. COMPARISON WITH RADIATION DAMPING.

It is interesting to see how the renormalizing procedure when applied to mesons compares with the much more drastic subtraction procedure of Heitler's (1941) theory of radiation damping*. Heitler's theory has been most successful when applied to the scattering and creation of mesons by nucleons. In the cases where ordinary perturbation theory gives a cross-section which increases with primary energy, the inclusion of Heitler's damping term gives a cross-section which decreases with primary energy. However, this situation does not arise in the scalar or pseudo-scalar meson scalar interactions, nor for the vector interaction of neutral vector mesons. (If it did occur, it would be only for longitudinal mesons, and Feynman (1949 b) has proved that the cross-section is zero in this case. The proof is given for photons and is applicable to neutral vector mesons. However, it depends on the cancellation of certain terms, some of which do not occur if the mesons are charged. But for charged vector mesons Dyson's procedure cannot be effectively applied.) Thus the renormalizing procedure is inadequate in all cases where an interesting comparison might have been made, and Dyson's theory, as here applied to meson-nucleon interaction, is not, as might have been hoped, in any important case an effective and preferable alternative to Heitler's.

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* This theory has been developed in numerous subsequent papers.

XVII. CORRESPONDENCE

Observation of Unimolecular Growth Steps on Crystal Surfaces.

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[Plates VII & VIII.]

AN extensive line structure on prism faces of beryl crystals has been revealed by microscopic observation. Evidence is given below to show that these lines represent steps only one unit cell in height; if this is the case the height of the step should be $9.17 \text{ \AA} \times \cos 30 = 7.9 \text{ \AA}$.

The appearance and behaviour of these lines are the same whether the face is examined in its untouched, natural state, or after the deposition of a highly reflecting thin film of silver on the face. The sole difference between the two cases is that the visibility of the lines is much higher when the surface has been silvered. These lines must therefore correspond to genuine geometric surface details.

As nearly as one can tell, these lines follow contour lines of the surface topography. The lines are widely spaced where the surface is relatively flat, and crowd together where there is a steep gradient. The only evident departure from contouring is that occasionally a single line terminates at a point in the face, instead of forming a closed loop. These lines must therefore represent steps on the surface. If the steps are taken to be one unit cell high, the point of termination must be interpreted as the end of a screw dislocation.

An exact survey of the surface topography by interferometric methods should permit of a direct measurement of the step height at each line. So far attempts to apply this method have only sufficed to show that the step height is less than $34 \text{ \AA}$. From the fact that no visible kink appears where an interference fringe crosses one of the lines, one may also infer that the step height is less than $20 \text{ \AA}$.

Further evidence will be presented below, in the discussion of fig. 3, that the lines represent steps all of the same height. The evidence thus points towards these steps being one unit cell high.

The observation under the microscope of such small steps was surprising, and so contrary to normal practice or prediction, that it was felt that further evidence was needed before the results could be reported. They were not, therefore, made public outside this Department. During

* Communicated by the Author.

the Bristol University Summer School on the Theory of Crystal Growth in September 1949, the theory of the behaviour of the steps originating from screw dislocations was developed much more fully by Frank, and it was seen that the correspondence was so exact between the predictions of this theory, developed for unimolecular steps, and the observations on beryl crystals, that one was led to the unavoidable conclusion that the observed steps were, in fact, only one unit cell high.

The technique used in observing these steps consisted in first coating the face to be examined with a film of silver of reflectivity some 70-90 per cent, the silver being deposited under conditions normally used for multiple-beam interferometry (thermal^{*} evaporation in a vacuum of pressure about 10^{-5} mm. Hg.). The surface was then examined in reflexion using a normal type of metallurgical microscope, bright field illumination being used with the field iris stopped down to give a fairly narrow illuminating beam, the specimen being racked slightly off focus.

By going slightly off focus when observing the surface, a phase difference is introduced between the diffracted wave fronts, and a certain intensity distribution is produced defining the position of the step edges. The precise nature of the intensity distribution is, of course, dependent on the position of the focal plane of the objective, non-complementary intensity distributions being produced on opposite sides of the true focal plane. In general, it has been found best to work with the edge imaged by an intensity distribution consisting of a broad minimum between two narrow maxima (see figures). These unimolecular step edges have been observed with objectives of N.A. ranging between 0.058 and 1.3, the visibility of the effect apparently decreasing with decreasing numerical aperture of the objective: it is, however, difficult to determine whether this decrease in visibility is primarily due to the decrease in the observing numerical aperture, considered as the collector of a cone of light of certain angle, or is caused, partly or entirely, by other factors dependent on the value of the numerical aperture.

The deposition of a reflecting silver layer, some 250-400 A.U. thick, greatly increases the visibility of the diffraction effect produced by the step edges. It does not seem to alter the nature of the intensity distribution in the image of the edges as obtained from an unsilvered face. This was to be expected from the evidence obtained from multiple-beam interferometry (Tolansky 1948) that such silver films, when deposited under correct conditions, contour the surface of the substrate to within very close limits.

It would seem probable that improvements could be made in the technique of observation which would further increase the sensitivity.

The topography of prism faces of beryl crystals is in general complex, with a tendency to form occasional low plateaux of a typical "razor-blade" shape, similar in outline to the outer loop of fig. 2. On the surface of two such main plateaux the two very simple cases shown in figs. 1 and 2 were found.

Fig. 1 (magnification $625\times$) shows the simplest case of a single screw dislocation, imaged here as a dot, from which runs a spiral edge, as predicted by the theory (Frank 1949 a). The *c*-axis of the crystal is here, as in all the figures, parallel to the almost straight edges. The light area is a region of very coarse structure, the general, irregular, and randomly distributed, surface markings being probably due to the deposition of foreign material after the beryl crystal had ceased to grow. This irregular and random marking is of general occurrence on faces of beryl, varying considerably in density.

Fig. 2 (magnification $1050\times$) shows the next most simple case, that of growth from the step joining a right and a left handed screw dislocation (Frank 1949 b). According to the theory unclosed loops like the inner one, attached to a pair of dislocations, extend during growth of the crystal in such a way as to generate successive closed loops, exemplified by the outer one. (The triangular area cutting into the closed loop probably consists of an over growth of foreign crystalline material). The two dislocations in this case are also imaged as dots, this being the usual type of imaging on these prism faces.

Figs. 3 and 4 show the more normal type of behaviour seen on beryl, the above simple cases being exceptional. In fig. 3 (magnification $625\times$) the steps advancing from the right are split into three sections by a succession of three crystal inclusions, which act as obstacles. Of the three sections, the central and lower sections first combine again to form a single section. (Counting from the last edge before division commences on the right, there are 37 edges in both the central and lower sections before junction occurs again. Similarly, considering the junction beyond the third obstacle, there are 57 edges in both the upper and lower sections between the first division of the edges and the first complete edge. It must, therefore, be that, in general, each step is a like unit step. For a step one unit cell high this type of behaviour is immediately understandable, and in fact necessary, but for steps of two or more unit cells it would appear very probable that in these circumstances the steps would either split into smaller units or combine to form multiple steps.

The slow closing in of the edges beyond any inclusion, and the rapid elimination of the re-entrant angle formed at the junctions of the different sections, is typical.

Fig. 4 (magnification $500\times$) shows the effect produced by a distribution of dislocations "dominated" by the steps originating from another group, far off the picture to the left. Some of its features are discussed by Frank, below.

Similar behaviour to that reported above has been seen on two other crystals of beryl, in these cases of typical emerald appearance and habit, while the above crystal was of aquamarine type. The three crystals came from widely different localities (*e.g.* the Urals and California), so that this would seem to be a general type of behaviour of beryl crystals..

FIG. 1.

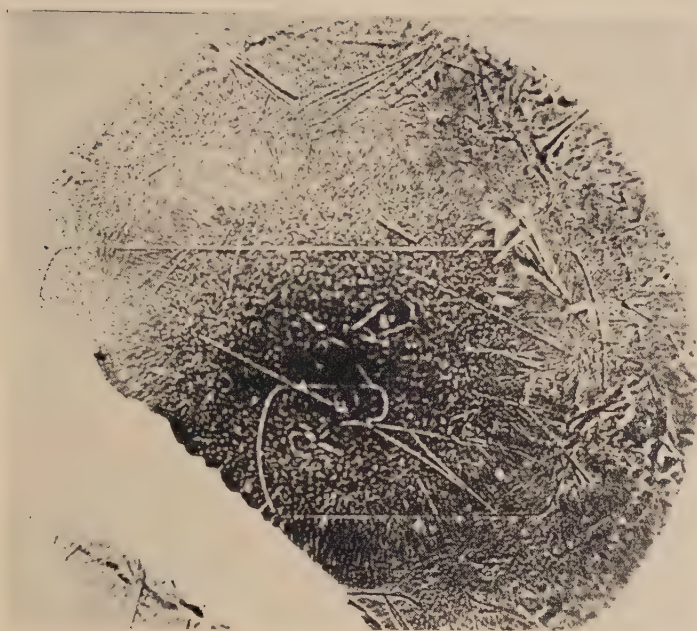


FIG. 2.



Figs. 1, 3 and 4 negative. Fig. 2 positive.

FIG. 3.



FIG. 4.



Taking into account the shortcomings of two-dimensional nucleation theory (Burton, Cabrera and Frank 1949, Cabrera and Burton 1949), the general validity of the dislocation theory of crystal growth would seem to be established. Further confirmation of the theory should be obtainable not only by observations of similar static phenomena on other types of crystals, but also by observing successive small amounts of growth or solution on faces of crystals, the topography of which had been previously determined. By this means a kind of cinematograph picture could be built up of the behaviour of the steps. In the case of beryl, further growth is not possible, but it is hoped to observe solution effects and thereby test the theory further.

Some small rod-like structures can be seen in the lower part of fig. 4. This rod type of structure is of common occurrence on the beryl crystals examined and occurs invariably on steep gradients running in the general direction of the *c*-axis. The rods are often found with one or more dislocations at their base and usually show a somewhat irregular step structure.

The difference in density of occurrence of screw dislocations per unit area can be considerable, both between different areas of the same face, and crystallographically equivalent faces of the same crystal. Thus there are some 100 screw dislocations in an area of 7.6×10^{-3} sq. mm. of one face, on other parts of which areas of several square millimetres show no sign of dislocations. An equivalent prism face of the same crystal shows no sign of dislocations over an area of several square centimetres. There is a definite tendency for dislocations to be closely spaced along lines either roughly parallel or perpendicular to the *c*-axis, as one would expect from general dislocation theory.

ACKNOWLEDGMENTS.

I am grateful to Professor S. Tolansky for his interest and encouragement during the course of this work. My thanks are due to the Mineralogy Department, British Museum, for the loan of several specimens; also to the Department of Scientific and Industrial Research for the provision of a maintenance grant.

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Note on the Structure of a Crystal Surface.

By F. C. FRANK,

H. H. Wills Physical Laboratory, Bristol*.

[Received December 23, 1949.]

THE observations reported by Griffin (1950) provide an unexpected direct confirmation of the theoretical conclusion that dislocations play an essential role in the growth of crystals. Indeed, they provide the first direct visual evidence of the existence of dislocations themselves. They also offer promise of a much closer insight into the actual conditions under which the growth of natural crystals occurred. If it also turns out that a similar technique will reveal details of "molecular" thickness on other crystals, growing in the laboratory, the possibilities for enlarging our knowledge about crystal growth processes are, of course, enormous.

The quantitative theory of crystal growth which has been developed in various papers by Burton, Cabrera and the writer (1949, 1950) (some of which, as yet unpublished, were presented at the Bristol Summer School on the Theory of Crystal Growth) has so far dealt mainly with crystals formed from spherical or cubic molecules, with growth occurring on crystal faces of high symmetry. In qualitative principle the theory applies equally, though with complications, to the $(10\bar{1}0)$ face of Beryl, studied by Griffin. There appears to be no reason to doubt that the essential building unit of Beryl is the Si_6O_{18} ring with its attendant two aluminium and three beryllium ions, making half the unit cell found by Bragg and West (1926). These units may be regarded as "pill-boxes", 7.9 Å. in diameter and 4.6 Å. in height, close-packed side by side in the basal planes of the crystal, and one on top of the other in the direction of the hexagonal axis. In this direction alternate Si_6O_{18} rings differ in orientation by 25° . This alternation secures the best coordination of oxygens about the cations, and doubles the X-ray unit cell, but may be considered a secondary detail of the building principles so far as we are concerned. On a $(10\bar{1}0)$ face these "pill-boxes" lie on their sides packed in flat layers in rectangular array, and growth would be expected to proceed by the spreading of such "monomolecular" layers by accretion of new units at their edges. At the low supersaturations essential for the growth of good crystals such layers would not develop on a free flat surface except from the points of emergence of dislocations with a component of the displacement vector normal to the surface ("screw dislocations" for short, though it is not essential that they should be pure screw dislocations). The way in which the edges of monolayers develop as "growth spirals" centred on the dislocations have been described elsewhere (Frank 1949), and beautifully illustrated in Griffin's figs. 1 and 2.

* Communicated by the Author.

The dependence of the two-dimensional crystal growth rate on the orientation of the step line imposes a characteristic distortion of the growth spirals and loops, exhibiting the symmetry of the crystal face. A fairly simple theory can be given to account for the shape assumed by each growth layer as it expands, the characteristic "razor-blade" shape seen on the beryl crystal being a typical example. In essence it is the same theory as was developed earlier (see for example, Friedel (1926)) for three dimensional crystal growth on the assumption that the growth rate at any point on a crystal surface depends only on the local crystallographic orientation of the surface, and its environment. We now appreciate that this is a far from correct assumption in that case, but in two dimensions it should be much more nearly true. In the latter case, a straight edge corresponds to a sharp minimum in the growth rate as a function of orientation. Truly sharp minima, and therefore truly straight boundaries are not in general to be expected. When the rate of advance, v , of the step, depends on its orientation ψ according to the law

$$v = v_0(1 + B\psi^2),$$

we can show that the resulting boundary will have a radius of curvature $(1 + 2B)$ times its distance from the centre of the figure. A simple theory, applicable in certain circumstances which are particularly likely to occur in growth from solution, makes the rate of advance v proportional to the number of "Frenkel kinks" in the step line. Then it follows that $B = e^{\phi/kT}/8$, where ϕ is a neighbour-neighbour interaction energy which we may take to be $\frac{1}{3}$ of the latent heat of solution. In this case the nearly straight edge of the razor-blade shape in Griffin's figure (2) has an apparent radius of curvature 100 times its distance from the centre, though it may be more (*i.e.* the apparent curvature is possibly due to optical distortion). Thus ϕ/kT is 6, or more. By contrast, the growth figures on a synthetic emerald grown hydrothermally by Nacken (1948) (Photographs by Griffin, not reproduced here) are similar, but have strongly curved edges to the "razor-blade" indicating $B=8$, whence $\phi/kT=4.16$. Supposing the natural and synthetic crystals grew from similar media, we may deduce that the absolute temperature of growth of the natural crystal was only about two-thirds Nacken's working temperature. Information of this is unfortunately lacking, but the indication that the natural crystal probably grew at a moderate temperature may be of interest.

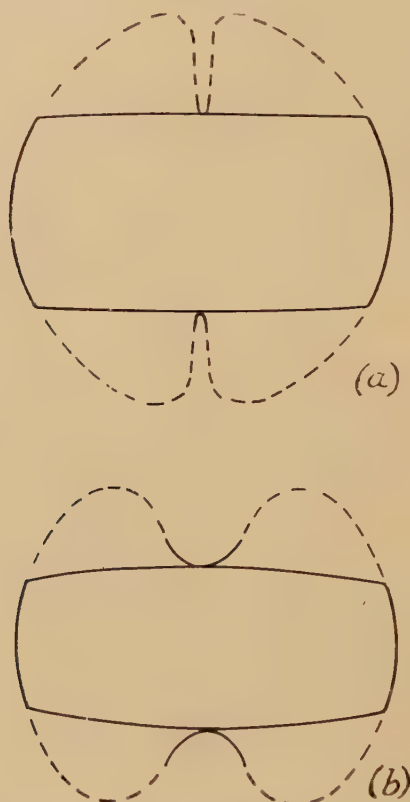
The two ends of the razor-blade are very nearly arcs of the same circle both for natural beryl and Nacken's crystals, indicating that the growth rate is practically independent of orientation for the range of orientations occurring in them ($\pm 30^\circ$ from the normal to the hexagonal axis in the case of the natural crystal).

Fig. 5* shows polar diagrams of two dimensional growth rate which

* Figures in this letter are numbered from 5 onwards to simplify reference to figures in Griffin's article, figs. 1 to 4.

would account for the observed two-dimensional growth figures. These polar diagrams are naturally uncertain for the range of orientations which do not appear in the figures: in such ranges one can only say for certain that the polar diagram lies outside the circles whose diameters are the lines connecting the centre to the corners of the figure.

Fig. 5.



The "razor-blade" outline of a growth layer on the $(10\bar{1}0)$ face of beryl (hexagonal axis horizontal) and the associated polar diagram of rate of growth as a function of boundary orientation, (a) for the natural crystal. (b) for Nacken's synthetic crystal. The form of the polar diagram is uncertain where represented by a dashed line and coincides with the "razor-blade" outline on circular arcs at the ends.

Observation of the spacing between turns of a growth spiral, or of its form where it joins the dislocation, enables us to measure a characteristic length, "the size of the critical nucleus", whose order of magnitude is $a\phi/kT\ln\alpha$ where a is a lattice spacing of the crystal and α is the saturation ratio. From fig. 2 this length is found to be about 1 micron, whence $\phi/kT\ln\alpha$ is about 10^3 . In conjunction with the former estimate of ϕ/kT we may deduce that the degree of supersaturation at which

growth took place was about 1 per cent. These estimates are not intended to be final or accurate, but are meant to indicate the kind of information which we should be able to derive from the type of observation Griffin has been able to make.

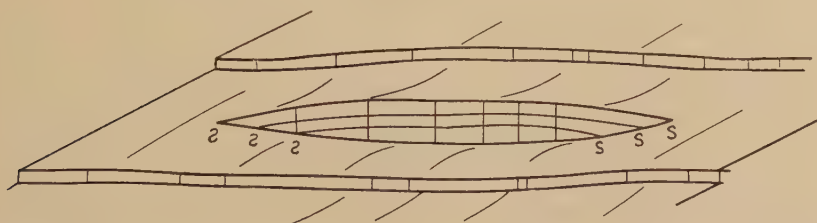
Whereas Griffin's figs. (1) and (2) show the simplest kind of growth initiation centres, he has other photographs showing initiation by larger groups of dislocations, such as occur in his fig. 4, though here they are not acting as an initiating group because they are "dominated" by a

Fig. 6.



Three successive stages in the passage of a dominating sequence of growth steps over a dislocation. Each line represents a unimolecular step, down to the right. The next stage in this succession will resemble the first.

Fig. 7.



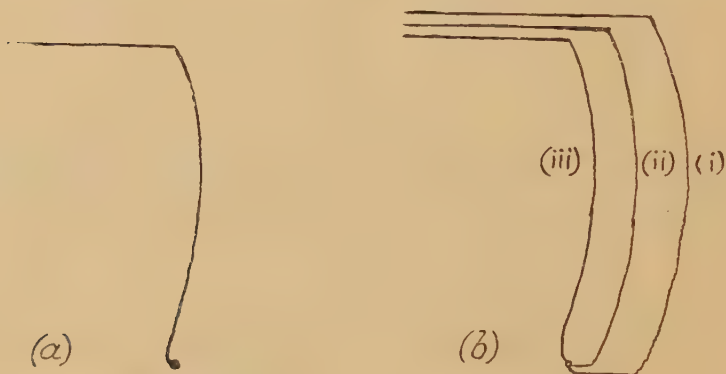
Schematic perspective sketch showing crystal surface with two unimolecular growth steps and a short shallow slip zone. The terminations of the latter provide three left-handed and three right-handed dislocations. Further growth (dominated by the step sequence) will produce a pattern corresponding to Griffin's fig. 4.

more active group lying off the picture to the left, in the way described by Frank (1949, b). The sketches in fig. 6 show three successive stages in the passage of a dominating sequence of growth fronts across a single dislocation, stages which may be recognized at various places in fig. 4. Fig. 4 also shows, as well as the randomly distributed dislocations, two groups lying approximately on a straight line, making a closely spaced row of right-handed dislocations at the top of the picture, and of left handed dislocations near the bottom. This is the kind of distribution of screw

dislocations which results from the formation of a limited slip-zone, as illustrated in fig. 7. One may readily see how subsequent growth on a surface of this configuration, under the domination of a close sequence of step-lines originating elsewhere, produces the general pattern of fig. 4.

It is interesting to consider the origin of such slip zones, and similar arrangements of dislocations to be found elsewhere in pictures taken by Griffin, in which, however, the line is parallel to the hexagonal axis, instead of transverse to it. A likely cause is the stress resulting from inhomogeneity of ionic replacement in the crystal. The fact that the crystal is coloured is sufficient evidence that ionic replacement occurs. A change in the composition of the solution will produce inhomogeneity in the crystal, which must evidently lead to lattice curvature. Now, consideration of the growth of a curved crystal from a mixed solution shows that it will suffer oscillations in the lattice spacing, with a wave length of the

Fig. 8.



(a) A form of growth front occasionally observed : (b) the normal form of growth spiral (i) is transformed into the shape (iii), with reversed curvature, as in 8(a), by a slight dissolution following normal growth.

order of magnitude of its shortest dimension, accompanied by considerable stresses. Dislocations already present may move under these stresses, but, additionally, the surface stress in new growing layers (particularly shear stress and tension) can, relatively easily, produce surface faults, which become true dislocations when buried under additional layers. This is probably the chief source of new dislocations, lineage boundaries and the like, in slowly growing crystals. Of course, the initial dislocations needed to make the first crystal seed capable of growth are generated with ease at the high supersaturation needed for nucleation.

On certain crystals, Griffin finds that the growth fronts have a reversed curvature near their terminations on dislocations, as in fig. 8(a). This appears to indicate that the last phase in the development of the crystal was a slight dissolution, before all change ceased. Fig. 8(b) shows how the

normal growth spiral (i), retracting in dissolution by way of stage (ii), proceeds to wind the spiral the other way, close to the dislocation, as in stage (iii) which corresponds to 8(a).

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Transfer Rates for Surface Films of HeII.

By E. J. BURGE and L. C. JACKSON,
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PUBLISHED measurements of the rate of transfer of HeII by the surface film fall into two groups. On the one hand there are the pioneer studies of Daunt and Mendelssohn (1939) which showed that the rate depends only on the smallest periphery above the liquid helium level and on the temperature, increasing from zero at the λ -point to a flat maximum of about 7.5×10^{-5} cm³/sec/cm. at 1.5° K. These observations were substantially confirmed by the work of Webber, Fairbank and Lane (1949) and the later work of Atkins (1949).

On the other hand Atkins in his earlier work (Atkins 1948 a) observed rates up to ten times those of Daunt and Mendelssohn and showing a marked dependence on the distance of the higher helium level from the rim of the beakers but independent of the distance between the two liquid levels. He used a capillary beaker terminating in a spherical bulb and the results were attributed to temperature gradients and possibly the geometry of the vessel.

Similarly de Haas and van den Berg (1949) have recorded high creep rates and a dependence of the rate on the difference between the helium levels. They found the rates of *emptying* the beaker were those to be expected for a syphoning process, *i.e.* dependent on the difference of height of the helium levels. This type of process will not, however, explain the rates of *filling* initially observed by Atkins, and confirmed later at Oxford and at Bristol (for contaminated surfaces), which were independent of the difference of height of the levels but dependent on the height of

* Communicated by the Authors.

the rim of the beaker above the highest helium level. Their experiments were carried out in the absence of radiation and they attribute the difference between their results and those of Daunt and Mendelssohn to this factor.

Bowers and Mendelssohn (1949) showed that absence of radiation had no effect on the normal creep rates, and that the high creep rates observed by Atkins in his first experiments were due to films of solidified gases (*e. g.* air) on the walls of the vessels. In his later experiments Atkins has confirmed the correctness of this explanation. It may be of interest to record our own observations on creep rates collected during the course of our experiments on helium II films (Jackson & Burge, 1949) and designed to test the similarity of our experimental conditions to those of Daunt and Mendelssohn in their measurements of creep rates and film thickness. These observations were made with a cylindrical beaker enclosed in the combined uniform temperature enclosure and radiation shield shown in

Fig. 1 (a)

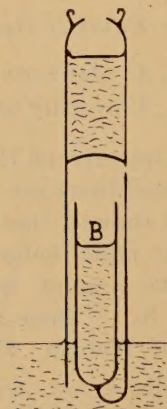


Fig. 1 (b)

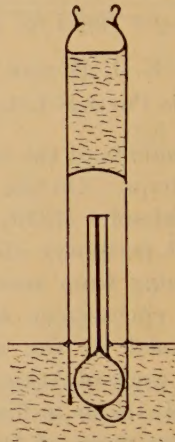
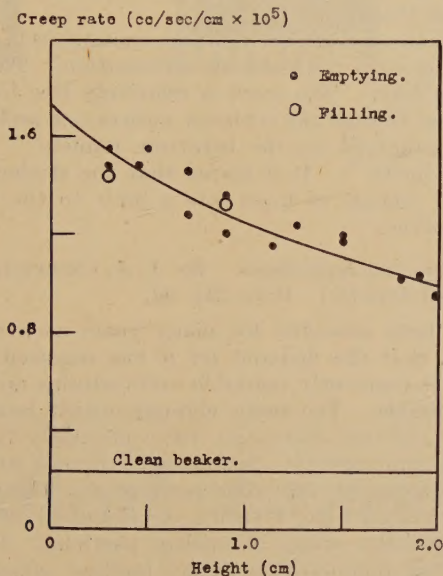


fig. 1 (a). The walls are silvered except for two narrow longitudinal slits. A half-watt neon lamp with a filter of Chance's ON19 glass served as the source of illumination. The creep rates agreed closely with those of Daunt and Mendelssohn.

After the publication of Atkins' first note (Atkins, 1948 a) the cylindrical beaker of fig. 1 (a) was replaced by one consisting of a glass capillary tube, length 2.2 cm., internal diameter, 0.04 cm. terminating in a spherical bulb of diameter 0.8 cm. fig. 1 (b). The creep rates observed again agreed very well with those of Daunt and Mendelssohn. The appearance of the note of Bowers and Mendelssohn led us to repeat our observations (1) with the "clean" Atkins type beaker, and (2) after admitting some 50 cm³ of air to the cryostat, a small portion of which condensed upon the beaker. The creep rate with the "clean" beaker was again normal but the maximum rate with the contaminated beaker was some seven times

greater and a marked variation with height was observed (fig. 2; $T=1.90^\circ\text{K}$). We confirmed Atkins' observations that the filling rates depended on the height of the rim above the highest helium level and not on the difference of the levels. In some of the experiments with the contaminated beaker the observations were continued until the levels of the liquid helium inside and outside the beaker were the same. The inner level was then found to overshoot and the oscillations first described by Allen and Misener (1939) and studied in detail by Atkins (1948 b) were observed. In one experiment twelve complete periods were timed, giving an average value for the period of oscillation of 10.4 secs.

Fig. 2.



Assuming the film thickness to be inversely proportional to the height and inserting the above value of the period of oscillation in the formula given by Atkins, the film thickness at a height of 1 cm. was calculated. The value obtained, $d=11.16 \times 10^{-6}$ cm. ($T=1.07^\circ\text{K}$) agrees well with the early results of Atkins. Unfortunately similar observations had not been made with the clean beaker.

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XVIII. *Notices of New Books and Periodicals received.*

Introduction to Atomic Physics. By S. TOLANSKY. Third Edition. [Pp. 371.] (Longmans Green.) Price 15s.

THE appearance of this text for the degree student is welcome because the second edition with its 1946 appendix was already somewhat out of date.

New sections on recent developments have been included in various subjects. The chapters on cosmic rays and the cyclotron type of machine have been brought more up to date and that on the nucleus has been enlarged. Of the two new chapters added, one deals entirely with the neutron and its properties; the second concerns nuclear fission and atomic energy.

It is in one way unfortunate for the author that some of the subjects dealt with are developing at so remarkable a rate that the information is already out of date, e.g., in the sections dealing with mesons and the photographic study of nuclear and electron tracks.

In our experience students have been almost unanimous in praising the second edition as a stimulating source of valuable information. They will continue to do so with the new edition. The work is relatively free from the faults that marred the first edition, though the reviewer notices one unfortunate statement on page 318 in the paragraph on the betatron, namely, "The mass increase limits the ultimate velocity". It is feared that the student will take this to mean that relativistic change of mass sets a limit to the energy obtainable, which, of course, is untrue.

H. H. P.

Ions, Electrons and Ionizing Radiations. By J. A. CROWTHER. (8th Edition.) [Pp. 322.] (Edward Arnold.) Price 21s. 0d.

THAT this work has been accepted for many years as a standard text-book is shown by the fact that the demand for it has required an eighth edition. One reason is that it is eminently readable and contains no information which is superficial or unreliable. The main changes which have been introduced since the last edition, eleven years ago, have naturally been in the field of nuclear physics and atomic energy. In this field there is such a wide choice of material that there is room for individual preference. The reviewer would like to have seen some reference to Powell's development of the photographic method for the quantitative study of nuclear particles. It is now ten years since he pointed out the potentialities of this method, which are now being so effectively exploited as to speed up the tempo of advance many times. On the other hand, one can welcome the author's refusal to throw on the scrap-heap descriptions of early discoveries in the vain hope of circumscribing completely the subject of atomic physics within the limits of a single volume. This point of view will be shared by many teachers, particularly those who, like the reviewer, have watched the subject develop through the past fifty years.

A. M. T.

Faraday's Discovery of Electromagnetic Induction. By T. MARTIN. [Pp. 160.] (London: Arnold.) Price 9s.

THE author of this very readable account of a great discovery and the events which led up to it is the editor of Faraday's diary published before the war. In a connected story, illustrated by excerpts and drawings from the diary, readers can catch some of the atmosphere of scientific investigation a century and more ago and sense the working of mind and intuition of a great experimenter.

[The Editors do not hold themselves responsible for the views expressed by their correspondents.]